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Report No. SRIC 70-6

IMPROVED INSTRUMENTATION FOR DETERMINATION OF EXHAUST GAS OXYGENATE CONTENT

Contract Nos. CPA 22-69-40 and CAPE 11-68

Annual Report March 1970

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PB 200 268

STANDARD TITLE PAGE FOR TECHNICAL REPORTS	1. Report No. CRC-APRAC-CAPE-11-68-3	2. Govt. Accession No.	3. Recipient's Catalog No.

Title and Subtitle

Improved Instrumentation for Determination of Exhaust Gas Oxygenate Content -- SRIC

5. Report Date: January 1971

6. Performing Organization Code

7. Author(s): Marvin L. Vestal; Allan G. Day III; and William H Johnston

8. Performing Organization Rept. No. SRIC 70-6

9. Performing Organization Name and Address

Scientific Research Instruments Corporation
6707 Whitestone Road
Baltimore, Maryland 21207

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Agency Name and Address

Coordinating Research Council, Inc.
30 Rockefeller Plaza, New York, N.Y. 10020; and
Environmental Protection Agency
Durham, North Carolina

13. Type of Report & Period Covered: Final -- March 1970

14. Sponsoring Agency Code: CRC-APRAC-CAPE-11-68

15. Supplementary Notes

16. Abstracts

This report deals with the prototype aldehyde analyzer built by Scientific Research Instruments Corporation (SRIC). With the instrument, called the AUTOSPECT, SRIC has been able to simultaneously analyze engine exhaust for 9 different oxygenates. Alothough the AUTOSPECT can be calibrated to determine almost any desired oxygenate, the current instrument is set to determine the 9 most prevalent aldehydes believed to be present in exhaust gas. Work on the AUTOSPECT is aimed at procedural improvements and reductions to a practical portable oxygenate analyzer. In addition to unburned hydrocarbons, carbon monoxide, and oxides of nitrogen, the exhaust of automotive vehicles contains small amounts of partially combusted materials known as oxygenates. The most prevalent class of oxygenate components are known as aldehydes. Aldehydes are odoriferous, in some cases irritating to the eyes, and potential sources of photochemical reactions conducive to the formation of smog.

17. Key Words and Document Analysis. (a). Descriptors

Pollution Control
Exhaust Gas
Oxygenates
odor
smog
photochemical

17b. Identifiers/Open Ended Terms

AUTOSPECT

17c. COSATI Field/Group: 21E; 13B; 21D

18. Distribution Statement

Releasable to the public

19. Security Class (This Report)	21. No. of Pages
UNCLASSIFIED	56
20. Security Class. (This Page)	22. Price
UNCLASSIFIED	$3.00

FORM NBS-867(1-70)

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ABSTRACT

Chemical ionization mass spectrometry is shown to be a powerful general tool for the analysis of trace oxygenates in exhaust emission; it provides an analytical tool for trace components over a dynamic range from 1 parts per billion (ppb) to 10,000 parts per million (ppm).

A prototype mass spectrometer employing the double focusing principle of Mattauch and Herzog and featuring fixed ion-collectors at integral masses over the mass range 1 to 128 has been constructed and is described. The fixed collectors make possible selection of any nine mass numbers in this range and provide full duty cycle for each measured peak with instrumental time constant significantly shorter than 5 seconds.

Theoretical application of the method and experimental application of the apparatus to the following oxygenated species in the concentration range of 30-1300 ppm has been made: formaldehyde, acetaldehyde, acrolein, propionaldehyde, acetone, crotonaldehyde, butyraldehyde, 2-butanone, n-valeraldehyde, 2-pentanone, 3-pentanone, ethyl-butyraldehyde, and benzaldehyde. It is shown that in all cases, analysis is feasible via the M + 1 ion (protonated parent compound) using reagent ion CH_5^+ except that, with this reagent, interferences occur for acrolein and crotonaldehyde necessitating the use of a different reagent for these species.

Calibration of the mass spectral apparatus for all the above compounds has been made. Sensitivity of response for the various compounds range from 5-108 millivolts per ppm of oxygenated compound. With the exception of the larger aldehydes this response is practically all due to the M+1 ion. In the case of the larger aldehydes loss of H_2O from the protonated molecule, forming the M-17 peak, is the dominant process.

Preliminary measurements were sufficiently encouraging that the breadboard stage was skipped and a prototype research unit was designed and built. Further work requires the redesign of one portion of electronics, optimization of operational parameters, tests in cooperation with Scott Laboratories on exhaust from a current model automobile under cyclic conditions, tests for other components such as NO_x, exploration of negative ion reactions and design of a simplified unit for optimum utilization by untrained personnel and at minimum cost.

INTRODUCTION

The goal of this research is the development of an instrumental method of analysis for oxygenated hydrocarbons in engine exhaust. This method is based on the combination of the chemical ionization technique developed by Field and coworkers combined with the direct reading mass spectrograph developed at Scientific Research Instruments Corporation[1]. A bibliography of publications on chemical ionization mass spectroscopy is given in the Appendix.

The theory of analysis by chemical ionization is presented in Chapter II of this report. This theory shows the enormous enhancement in sensitivity and specificity which is possible with chemical ionization as compared to electron impact ionization.

The prototype system combining chemical ionization with the direct reading mass spectrograph for the rapid, continuous analysis of oxygenated hydrocarbons in engine exhaust is described in Chapter III. This prototype system employs a chemical ionization source which may be operated at source pressures as high as 10 torr. Mass analysis is performed using a small Mattauch-Herzog type double-focusing mass spectrometer. Fixed collectors are provided for each mass in the range from 1 to 128 amu. Any nine of these masses may be monitored continuously using nine independent electrometers and readout channels.

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(1) This method is covered by patent rights of Esso Research and Engineering Company with exclusive license to Scientific Research Instruments Corporation, Baltimore, Maryland.

Chemical ionization measurements have been conducted on a series of the aldehydes and ketones identified by Oberdorfer[2] as the more abundant oxygenated species occurring in engine exhaust. The compounds studied include formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, iso-butyraldehyde, n-valeraldehyde, iso-valeraldehyde, ethyl butyraldehyde, acrolein, crotonaldehyde, benzaldehyde, acetone, butanone, 2-pentanone, and 3-pentanone. These experimental results show that the technique should be capable of detecting most of the oxygenated hydrocarbons at levels from 300 parts per million down to 10 parts per billion in engine exhaust using methane as a chemical ionization reagent. With the exceptions of acrolein and crotonaldehyde no interference from other compounds in engine exhaust is indicated by our data taken in conjunction with the results of other investigations described in the literature. In the case of acrolein the crotonaldehyde some interference from hydrocarbons is encountered when methane is used as the reagent.

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(2) P.E. Oberdorfer, "The Determination of Aldehydes in Automobile Exhaust Gas," Paper 670123 presented at the SAE Automotive Engineering Congress, Detroit, Michigan, January, 1967.

EXHAUST GAS ANALYSIS BY CHEMICAL IONIZATION MASS SPECTROMETRY

General

Chemical ionization mass spectrometry produces ionic derivitives of the compound whose analysis is required by a sequence of reactions involving:

1. Electron impact ionization of a reagent gas.

2. Ion-molecule reactions of the reagent gas to produce a set of reagent ions that are stable with respect to further reaction with the reagent gas.

3. Reaction of the reagent ions with the compound whose analysis is required to produce ions characteristic of this compound.

By contrast, conventional mass spectrometric analysis involves direct ionization of the unknown by electron impact at pressures sufficiently low that collisions of the resulting ions with molecules do not occur. Thus if we denote the reagent gas by M, the stable reagent ions by R^+, and the substance to be analyzed by X, we have the following ionization mechanisms:

A. Chemical Ionization

$$M + e \longrightarrow M_i^+ + 2e \qquad (1)$$

$$M_i^+ + M \longrightarrow R^+ + N_i \qquad (2)$$

$$R^+ + X \longrightarrow X_i^+ + R \qquad (3)$$

B. Direct Ionization $X + e \rightarrow X_j^+ + 2e$ (4)

In these ionization mechanisms, M_i^+ represents the set of reactive ions of reagent gas M, N_i is a set of neutral products that need not concern us further, R^+ is a reagent ion (or set of reagent ions), X_i is the set of ions characteristic of the unknown and the reagent gas, and X_j^+ is the set of ions characteristic of electron impact ionization of the unknown X.

Note that in the case of chemical ionization the set of ions X_i^+ is produced without the simultaneous ejection of an electron that occurs in the direct ionization of X to form the set of ions X_j^+. This is a very important difference in the two types of ionization since the absence of a free electron in (3) imparts much more severe energy restrictions to this reaction than is the case for (4). The net result is that one expects the set of ions X_i^+ to be a much simpler set than X_j^+; in fact, one can envision systems in which X_i^+ is a single ion, a situation practically never obtaining for the set X_j^+ produced by (4). These expectations have been confirmed by many experiments utilizing a number of reagent ions, so that there is no doubt that chemical ionization mass spectrometry provides the analyst with a much simpler mass spectrum to interpret. This greater simplicity, in turn, leads to more reliable identification of the unknown compounds present in any system to be analyzed.

Sensitivity

In addition to simpler mass spectra, chemical ionization mass spectrometry is a considerably more sensitive method of analysis for compounds present at the part-per-million (ppm) level in a gaseous mixture. Consider, for example, an unknown X present at a concentration level of 1 ppm in some carrier gas. If we were to analyze for X with conventional electron impact mass spectrometry we would envision the following conditions:

Total ion-source pressure, $P_T \leq 10^{-5}$ torr.

Concentration of sample in ion source, $n_T = 3 \times 10^{16} P_T$ (molecules/cm^3, for P_T in torr).

Electron currents $I_e \leq 1$ ma $= 10^{-3}$ amperes.

Electron impact ionization cross-section $\sigma_i \approx 10^{-15}$ cm^2. (nominal value for 70 ev electrons)

Electron path in ion source, $L_e \approx 1$ cm.

- Detection efficiency, $E \approx 1\%$ (efficiency with which ions produced in the source are transmitted through the mass analyzer and detected at the ion collector).

Under these conditions the total ion current detected is given by

$$I_T = \sigma_i \, n_T \, I_e L_e E \qquad (5)$$

$$= 10^{-15}(cm^2) \cdot 3 \times 10^{11}(cm^{-3}) \cdot 10^{-3}(\text{amperes}) \cdot 1(cm) \cdot 10^{-2}$$

$$= 3 \times 10^{-9} \text{ amperes}$$

The total ion current for the unknown X present at a concentration level of 1 part per million is given by

$$I_x = 10^{-6} I_T = 3 \times 10^{-15} \text{ amperes} \qquad (6)$$

This current is normally distributed among a number of fragment ions produced by electron impact ionization.

The total ionization efficiency in the electron impact ionization can, in principle, be increased by increasing the electron current, the ion source pressure, or the detection efficiency. However, the maximum ion current which can be handled in most mass analyzers without introducing non-linearity due to space charge effects is about 3×10^{-9} amperes. Therefore, little additional enhancement in sensitivity can be obtained by increasing the total ionization efficiency.

In chemical ionization mass spectrometry the total pressure in the ion source is typically about 1 torr. The intensity of the primary ionization to produce the ions M_i^+ according to reaction (1) is still given by Equation (5). As can be seen from Equation (5) above, much smaller values of either electron current or detection efficiency can be employed while still realizing the maximum total ion beam that can be utilized in the mass analyzer. As a result, the small orifices required in the chemical ionization source to obtain high pressures do not limit the sensitivity of the technique since more than adequate electron beams and ion beams can be transmitted through the necessary orifices.

In chemical ionization the reagent ion intensity is given by

$$I(R^+) = I_T \left(1 - e^{-\sigma_2 n_T L_i}\right) \tag{7}$$

where I_T is given by Equation (5), n_T is the concentration of reagent gas in the ion source, σ_2 is the cross-section for the ion-molecule reaction ($\sigma_2 \geq 10^{-15}$ cm^2), L_i is the average ion travel distance in the ion source ($L_i \approx 1$ cm). The exponent in equation (7) may be expressed by

$$\begin{aligned} \gamma &= \sigma_2 n_T L_i = 3 \times 10^{16} \sigma_2 P_T L_i \\ &\geq 3 \times 10^{16} (10^{-15}) (1) P_T = 30 P_T \end{aligned} \tag{8}$$

where P_T is in torr. Thus the ions initially produced by electron impact (M_i^+) are quite completely converted to reagent ions (R^+) if the ion source pressure is a few tenths of a torr or more, and $I(R^+) \approx I_T$.

If X is at a sufficiently low concentration that its ionization by reaction (3) does not significantly deplete the concentration of reagent ions, it is easily shown that the ion current produced from the species X is given by

$$I(X) = I(R^+) \cdot \left(1 - e^{-\sigma_3 n_X L_i}\right) \approx I_T \left(1 - e^{-\sigma_3 n_X L_i}\right) \tag{9}$$

Where n_X is the ion source concentration of X (molecules/cm^3), σ_3 is the cross-section for reaction (3), and L_i is the ion path length.

At low sample concentrations, $\sigma_3 n_X L_i << 1$, and equation (9) reduces to

$$I_X = I_T \cdot \sigma_3 n_X L_i \qquad (10)$$

Experimentally, the value of $\sigma_3 L_i \geq 10^{-15}$ cm^3 for many of the ion molecule reactions involved. For an ion source pressure P_T, and a concentration of X of 1 ppm, Equation (10) becomes:

$$I_X = I_T \cdot 3 \times 10^{16} P_T \cdot 10^{-6} \text{ (molecules/cm}^3\text{)} \cdot 10^{-15} \text{ (cm}^3\text{)} \qquad (11)$$

$$= 3 \times 10^{-5} P_T \cdot I_T$$

Comparing with Equation 6 we see that

$$\frac{I_X \text{ (CHEMICAL IONIZATION)}}{I_X \text{ (ELECTRON IMPACT)}} \cong 30 P_T \qquad (12)$$

for the same total ion current, at the maximum operating pressure of the prototype chemical ionization system (10 torr) chemical ionization is at least 300 times as sensitive as electron impact ionization in terms of the ion current produced from a trace component for a given total ion current.

Linearity

The ion current produced from reactive species X in the reagent gas is given by Equation (9). At low concentrations the ion signal is directly proportional to concentrations of X as given in equation (10). For Equation (10) to be valid within 5%, it is required that

$$\sigma_3 n_X L_i \leq 0.05$$

$$n_X \leq 5 \times 10^{13} \text{ molecules/cm}^3 \qquad (13)$$

at higher concentrations a significant fraction of the reagent ions are destroyed by reaction, and the exponential equation (9) applies rather than the linear equation (10). The implications of this analysis of sensitivity and linearity is summarized in Table I.

Application to Engine Exhaust Gas Analyses

The specific problem to be solved in these analyses is to measure oxygenated hydrocarbons at low concentrations in a complex mixture of gases, the principal component of which is nitrogen. Nitrogen, the natural carrier gas of this complex mixture, is not itself a suitable reagent gas for the analysis of oxygenated hydrocarbons. A suitable reagent gas must, therefore, be added to the mixture. At first sight this might seem to involve a serious dilution of the sample. However, the fact that molecular nitrogen ions will undergo charge transfer reactions with practically any reagent gas we would envision easily circumvents this difficulty. For example, suppose methane, having reagent ions CH_5^+ and $C_2H_5^+$, had been added to the mixture as the reagent gas. Any electron impact ionization of the nitrogen will be followed rapidly by

$$N_2^+ + CH_4 \longrightarrow CH_4^+ + N_2 \qquad (14)$$

and

$$N_2^+ + CH_4 \longrightarrow CH_3^+ + N_2 + H \qquad (15)$$

TABLE I. SENSITIVITY AND LINEARITY OF CHEMICAL IONIZATION ANALYSES AS A FUNCTION OF TOTAL ION SOURCE PRESSURE

Pressure (torr)	Minimum Detectable Concentration (parts per billion)(1)	Maximum Allowable Concentration (parts per million)(2)
0.2	150	7,500
0.5	60	3,000
1.	30	1,500
2.	15	750
5.	6	300
10.	3	150
20.	1.5	75
50.	0.6	30
100	0.3	15
200	0.15	7.5
500	0.06	3
1,000	0.03	1.5

(1) Corresponding to 3×10^{-15} amperes mass analyzed ion current for trace species and 3×10^{-9} total mass analyzed ion current.

(2) For deviation from linearity $\leq 5\%$.

thus producing the same principal active ions of methane that will follow electron impact ionization of methane. These ions will not react with molecular nitrogen but will react rapidly with methane to produce the normal reagent ions CH_5^+ and $C_2H_5^+$. Therefore, with the exception of production of a slightly different ratio of reagent ions, ionization of the nitrogen is equivalent to ionization of reagent gas and there is no loss of sensitivity.

The basic nature of the oxygenated compounds to be analyzed suggests that a particularly appropriate chemical ionization reaction is that of proton transfer from a suitable reagent ion to the oxygenated hydrocarbon, viz:

$$XH^+ + \begin{matrix} R \\ R \end{matrix}\!\!\searrow\!\!\swarrow C=O \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!\searrow\!\!\swarrow C\text{-}OH^+ + X \qquad (16)$$

This reaction will occur readily for any hydrogen containing reagent ion provided that

$$P(\begin{matrix} R \\ R \end{matrix}\!\!\searrow\!\!\swarrow C=O) > P(X)$$

where P(X) is the proton affinity of compound X. Of course, if the proton affinity difference is too great the exoergicity of the reaction may result in considerable fragmentation of the ion $\begin{matrix} R \\ R \end{matrix}\!\!\searrow\!\!\swarrow C\text{-}OH^+$. Some fragmentation may be desirable for clarity of identification when mass interference occurs, but, in general, extensive fragmentation is to be avoided. The choice of reagent gas is thus directed towards one having reagent ions XH^+ such that $P(X) < P(\begin{matrix} R \\ R \end{matrix}\!\!\searrow\!\!\swarrow C\text{-}O)$ but with ΔP being as small as possible.

Ideally, the reagent gas should produce reagent ions that would not protonate other compounds in the gas mixture, such as olefins, aromatics, paraffins, carbon monoxide, etc. Although some selectivity in this regard is possible, complete selectivity of protonation of oxygenated hydrocarbons will not, in general, be possible. Hence, we must choose a reagent gas whose reagent ions and product ion produced by reaction with other species present do not by mass interference obscure the protonated forms of the oxygenated hydrocarbons.

These considerations lead to the conclusion that methane, with reagent ions CH_5^+ and $C_2H_5^+$ (M/e 17 and 29, respectively), is a reasonably good initial choice for a reagent gas for the oxygenated hydrocarbons. The pertinent chemical ionization reactions are the following:

$$CH_5^+ + \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C\text{-}OH^+ + CH_4 \qquad (3A)$$

$$C_2H_5^+ + \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C\text{-}OH^+ + C_2H_4 \qquad (3B)$$

$$C_2H_5^+ + \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O \longrightarrow \begin{matrix} R \\ R'' \end{matrix}\!\!>\!C{=}O^+ + C_2H_6 \qquad (3C)$$

where, depending on the specific energetics, dissociation of the ionic products may occur to some extent. Chemical ionization spectra for methane reagent reacting with a number of aldehydes and ketones are presented in Chapter IV.

THE PROTOTYPE SYSTEM

The prototype system for analysis of oxygenated hydrocarbons in engine exhaust gases consists of a chemical ionization source coupled with a direct reading mass spectrometer. A heated gas inlet system is provided for interfacing between the exhaust gas sampling point and the inlet of the mass spectrometer. A schematic diagram is given in Figure 1 of the ion optical system for the combination of the chemical ionization source with the direct reading mass spectrometer.

The mass analyzer employs the Mattauch-Herzog double focusing geometry with a 6" radius electrostatic analyzer and a fixed collector for each mass from 1 to 128 amu. This system was designed to be operated normally in the direct reading mode in which a selected set of masses are monitored continuously. However, provisions for electrically scanning to mass 250 are included in the design and scanning has been used during the initial exploratory research.

The chemical ionization source and differential pumping systems are designed to operate at source pressures as high as 10 torr for efficient chemical ionization of the oxygenated hydrocarbons of interest. With these high ion source pressures, the pumping system maintains the pressure in the ion source housing at a suitably low pressure (typically 10^{-4} torr) to avoid electrical breakdown. The analyzer section is isolated from the source section by a differential pumping slit and maintained at sufficiently low pressure (typically $< 10^{-6}$ torr) to avoid degradation of performance by ion-molecule collisions in the analyzer. Sufficient testing has been accomplished to assure that the differential pumping requirements are met by the

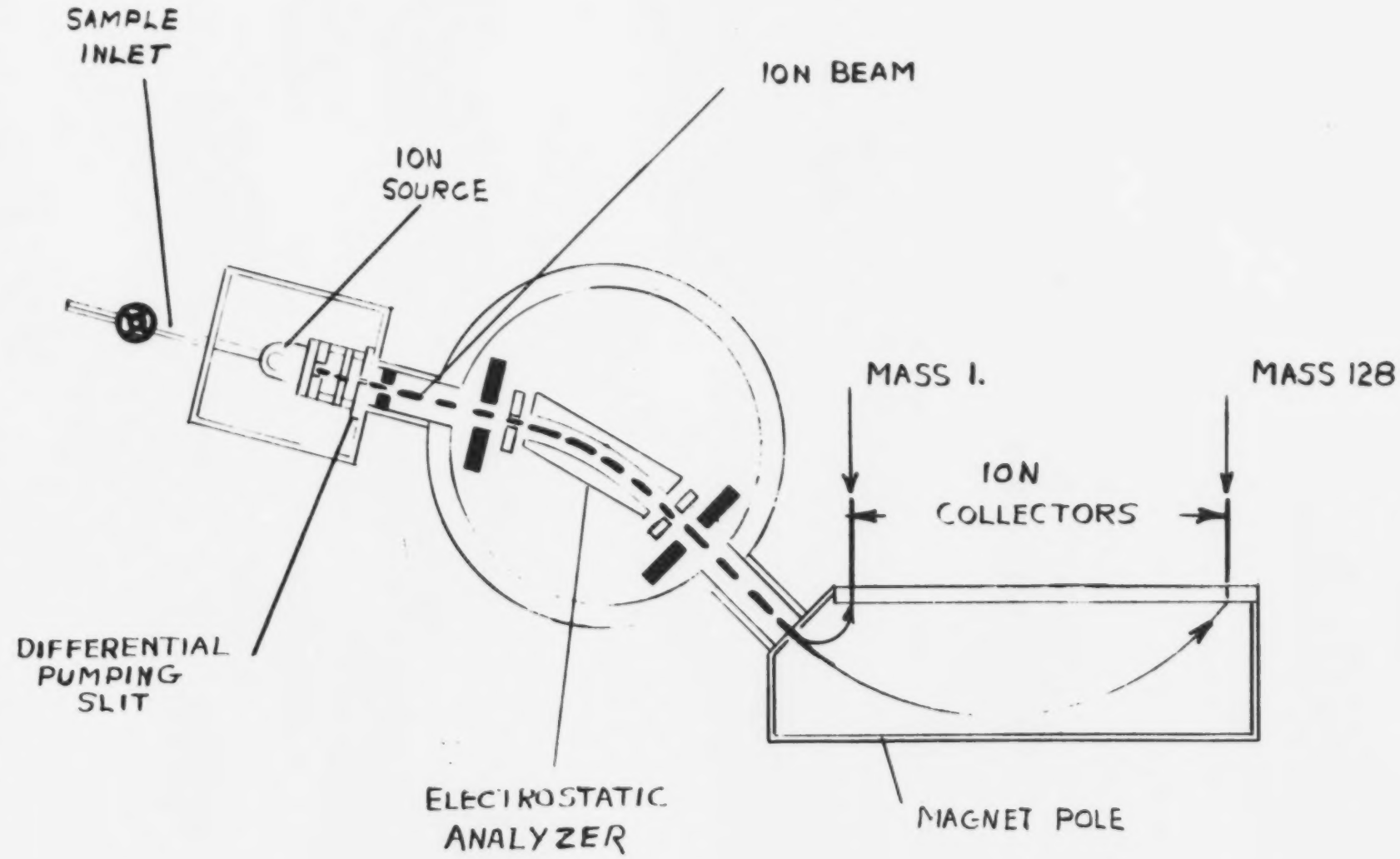


Figure 1. Schematic Diagram of the ion optics for the chemical ionization exhaust gas analyzer.

present design. Heaters are provided for the chemical ionization source and the glass inlet lines to allow operation at temperatures from 100°C to 350°C to minimize the anticipated problems in accurately sampling the raw engine exhaust.

In Figure 2 a pictorial sketch is given showing the relative locations of the principle components of the system. The ion source housing and electrostatic analyzer housing are separately pumped by high speed 4 inch diffusion pumping systems located as shown in Figure 2. The mechanical pumps backing the diffusion pumps are located in the bottom of the cart supporting the mass spectrometer. This cart is mounted on heavy duty casters and contains the complete mass spectrometer inlet system and pumping systems. The electronics for the system are located in a separate caster-mounted cabinet. The complete system is designed to be readily mobile.

A photograph of the principal components of the chemical ionization direct reading mass spectrometer is shown in Figure 3. These components are contained within the vacuum housing shown schematically in Figure 2 in the relative locations within the system shown in Figure 1.

A photograph of the completed prototype system is shown in Figure 4. The electronics cabinet on the left in Figure 4 contains all of the readout and control systems for the prototype unit. The cart on the right contains the direct reading mass spectrometer with chemical ionization source and the associated vacuum systems and sample inlet system.

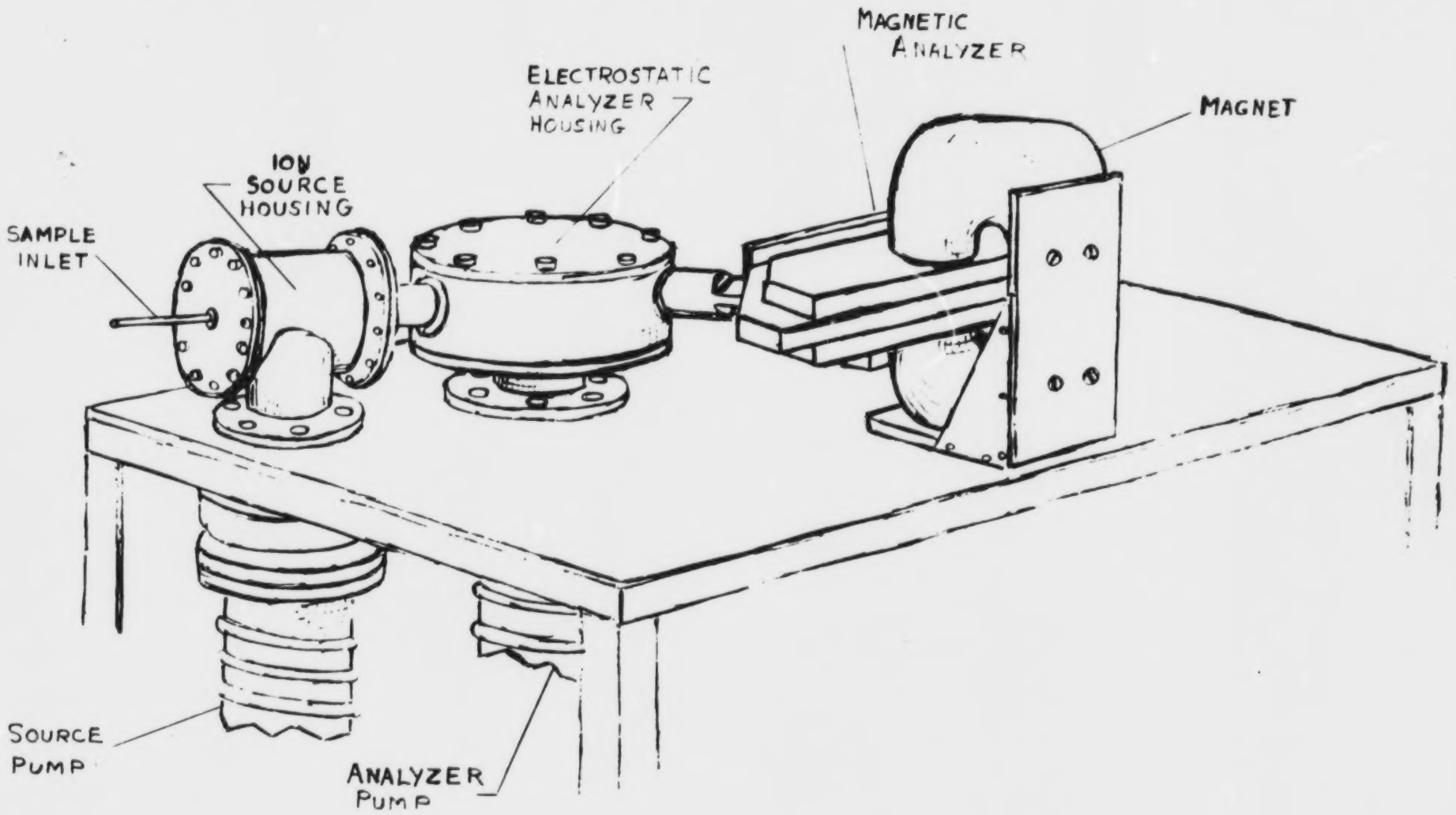


Figure 2. Pictorial sketch showing relative locations of the principal components of the chemical ionization exhaust gas analyzer.

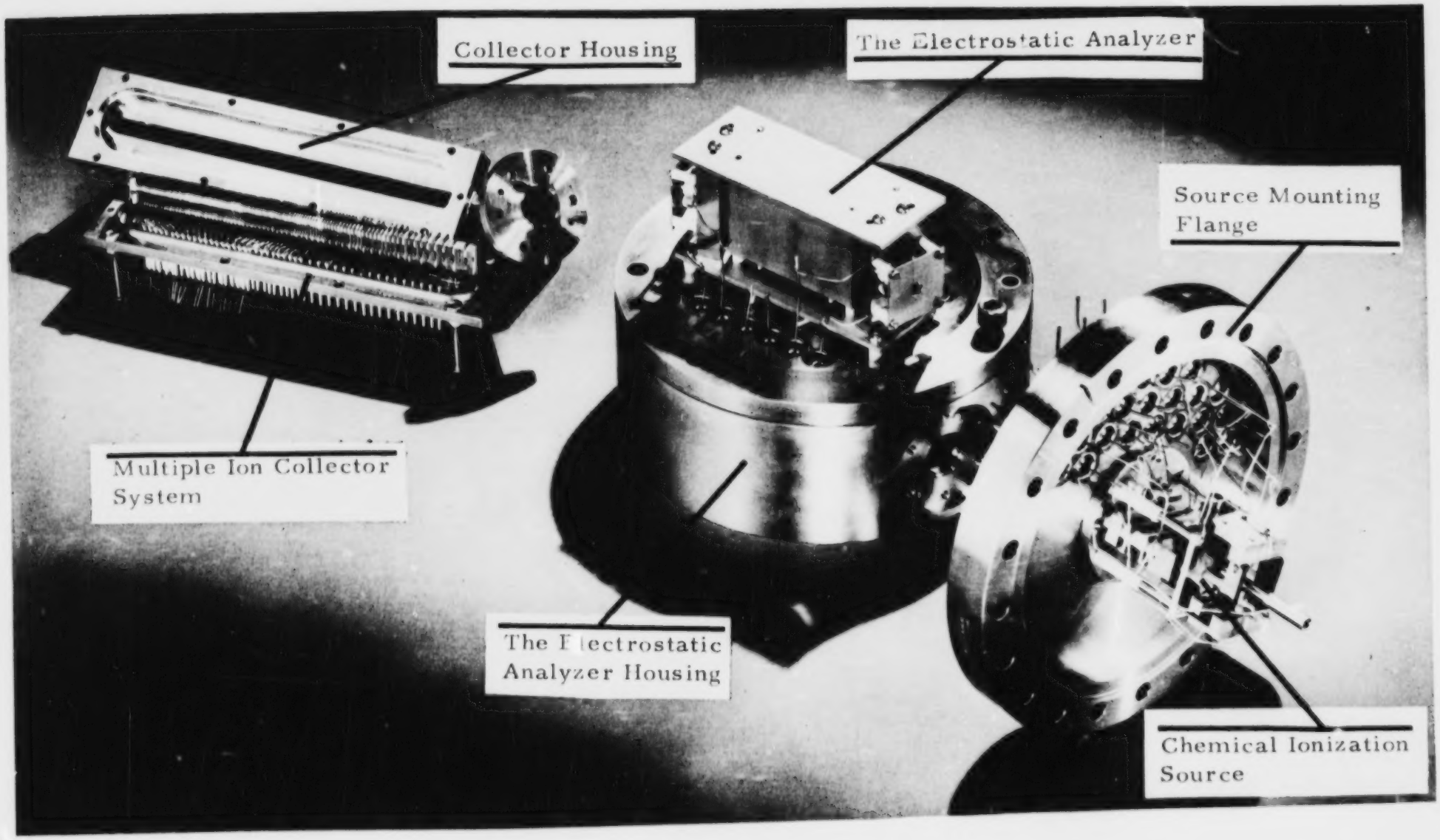


Figure 3. Components of the High Pressure Ion Source Electrostatic Analyzer and the Ion Collector System for the Chemical Ionization - Direct Reading Mass Spectrometer System.

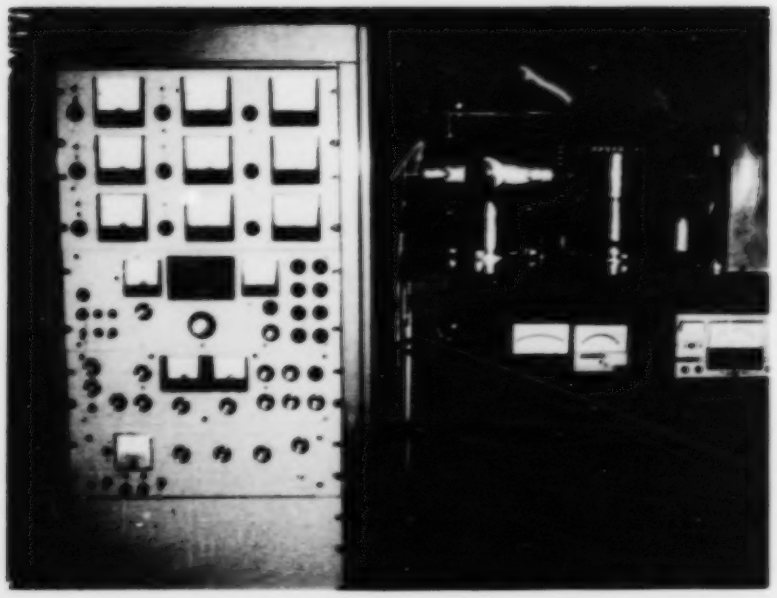


Figure 4. A Photograph of the Completed Prototype System.

The electronics cabinet on the left contains all of the readout and control systems and the cart on the right contains the direct reading mass spectrometer with chemical ionization source and associate vacuum systems and sample inlet systems.

Chemical Ionization Source

The chemical ionization source was designed to allow both chemical ionization and electron impact ionization with the prototype system. A detailed diagram of the chemical ionization source is shown in Figure 5. This source design is very similar to the conventional Nier type ionization source for a magnetic mass spectrometer with several detailed modifications to allow its use for chemical ionization.

The sample flows into the source through a hole in the repeller. The repeller and electron trap are sealed to the source block by ceramic washers to minimize extraneous leaks of gas from the source. The only substantial gas flows out of the source are through the orifices provided for the entrance of the electron beam and the exit of the ion beam. The electron beam entrance is a 0.020" diameter hole and the ionization exit is a slit 0.002" x 0.125". The electron beam is magnetically collimated using a 200 Gauss source magnet built up from Alnico V bar magnets and soft ion pole pieces. The electron emitting filter is a Rhenium ribbon 0.001" thick by 0.030" wide welded to 0.040" diameter molybdenum. The other metal parts in the ionization source are fabricated from Inconel 600 alloy and the ceramic insulators are high alumina ceramic.

Heaters for the source and sample inlet lines are provided and the system is bakeable to 350°C. The final slit in the ionization gun is sealed to a baffle separating the source and the electrostatic analyzer housings. This slit is 0.005" x 0.125" and constitutes the only substantial gas flow orifice between the two housings. These two housings are separately pumped by 4" oil diffusion pumps backed by 140 litre

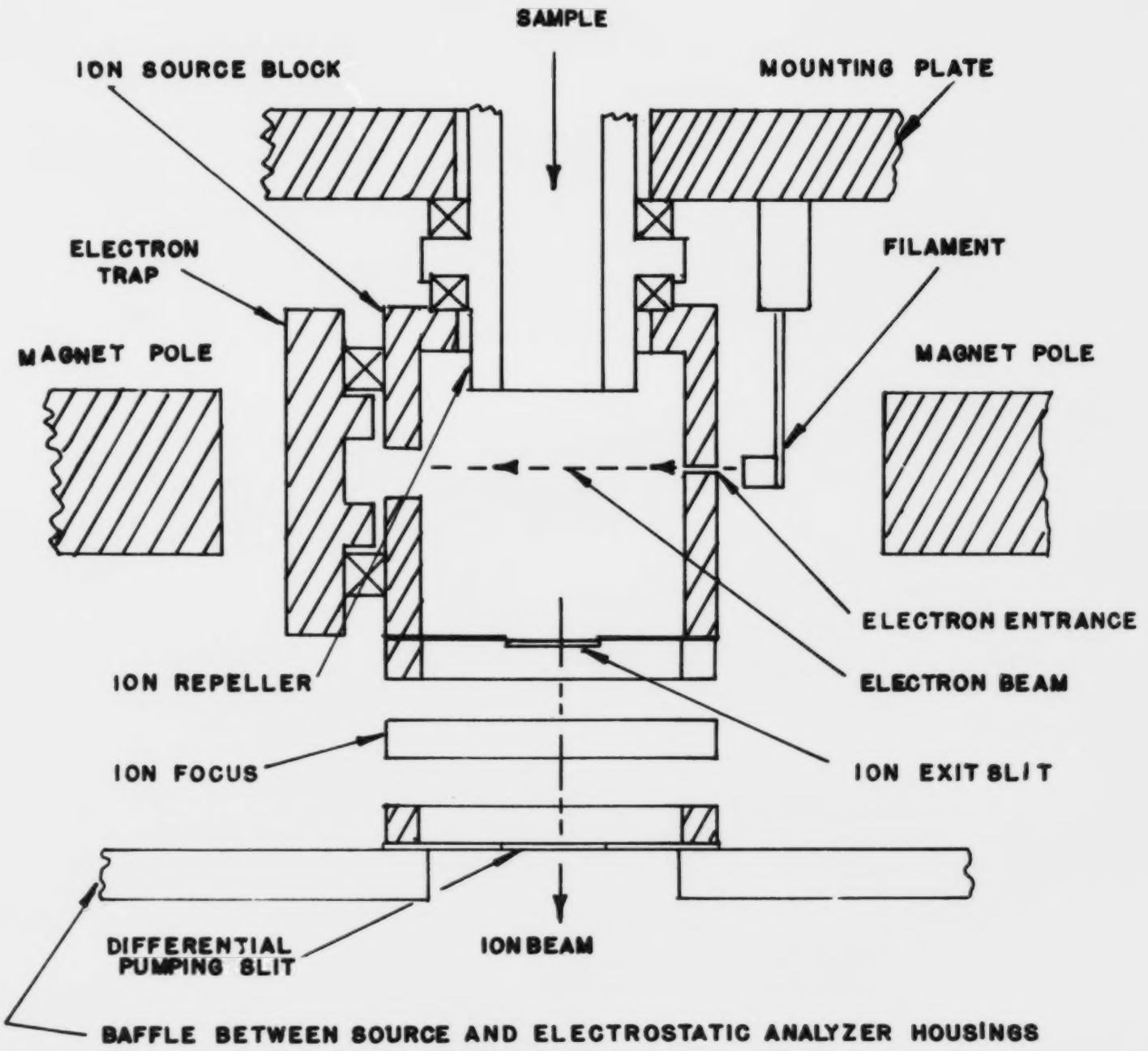


Figure 5.
Schematic Diagram Of The Chemical Ionization Source For The Prototype System For Analysis Of Oxygenated Hydrocarbons In Engine Exhaust.

per minute mechanical pumps. This differential pumping system allows operation with source pressures as high as 10 torr while maintaining the source housing at pressure below 10^{-3} torr and the electrostatic analyzer housing below 10^{-6} torr. Total ion beams in excess of 10^{-9} amps have been obtained with this ionization source.

Direct Reading Mass Spectrometer

The mass spectrometer is based on the original Mattauch-Herzog design of a double focusing mass spectrometer. The electrostatic analyzer is a 6" radius cylindrical condenser providing a deflection angle of 31.8°. This assembly is constructed of Inconel 600 and high alumina ceramic insulators and is bakeable to 350°C. An Alnico V permanent magnet provides a uniform magnetic field of 3500 Gauss across a half-inch gap. The Mattauch-Herzog geometry was chosen because it is double focusing for all masses simultaneously. The foci for individual masses fall in a precisely determinable plane and the location along the plane is proportional to the square root of the mass. This view allows the precise a priori determination of the relative locations for collectors for specific individual masses.

The principal unique feature of the mass analyzer is the multiple collector array used as a substitute for the traditional photo-plate detector in the Mattauch-Herzog geometry. This collector assembly consists of separate detectors for each unit mass in the range from mass 1 to mass 128 amu. A close-up photograph of the detector assembly is shown in Figure 6. An electrical connection from each collector is brought out through a vacuum feedthrough to a connector

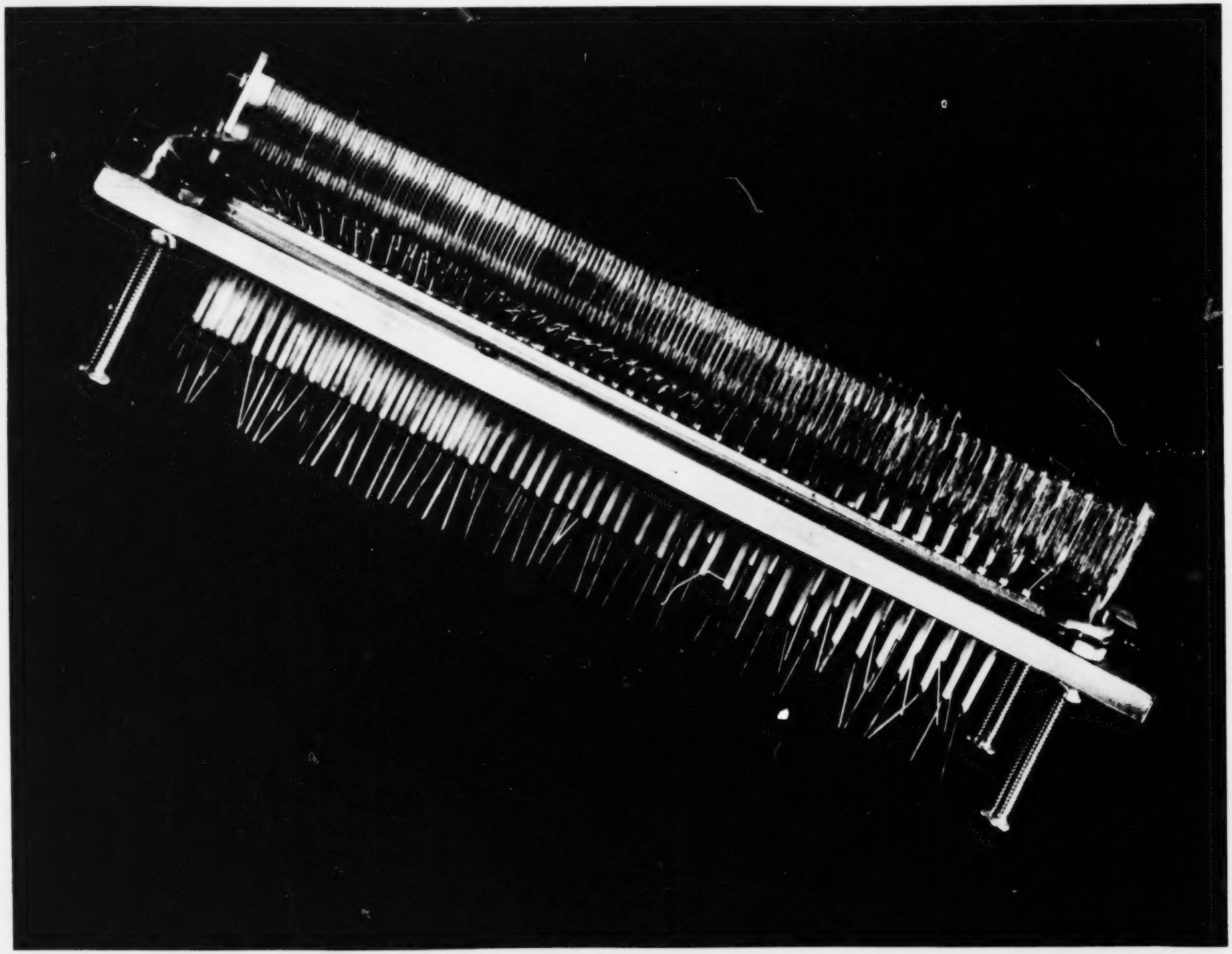


Figure 6. Close-Up View of the Ion Collector System

panel. This connector panel, which is similar to a miniature telephone switchboard, provides the means for selecting the masses which are monitored. Ten output channels are provided each consisting of a solid state electrometer mounted on the switchboard panel and a meter readout located on the front panel of the electronics cabinet as shown in Figure 3. The full scale sensitivity of these channels is continuously adjustable over a 1000:1 range from the front panel. Individual mass collectors selected for monitoring are connected to the input of one of the electrometers through a short jumper wire. The unused collectors are grounded by the use of special grounding clips provided. By merely rearranging the jumpers on this switchboard the set of masses monitored can be changed to correspond to a particular measurement.

Sample Inlet System

The sample inlet system for chemical ionization measurements on exhaust gases is shown schematically in Figure 7. This system is designed both for monitoring of actual exhaust gas samples directly from vehicle exhaust and for calibration of the system using artificial exhaust gases. The entire system through which exhaust gases pass is surrounded by a heating jacket which will maintain the system at approximately 150°C. An infusion pump and syringe is provided for controlled injections of calibration samples into the gas flow. The gas flow rate is monitored by a mass flow meter. A glass manifold is provided for coupling between the main flow of exhaust gas and the chemical ionization mass spectrometer. The glass manifold is designed to operate at a nominal absolute pressure of 1/2 atmosphere. A small sample of the exhaust gas stream is drawn off into this manifold through a fixed

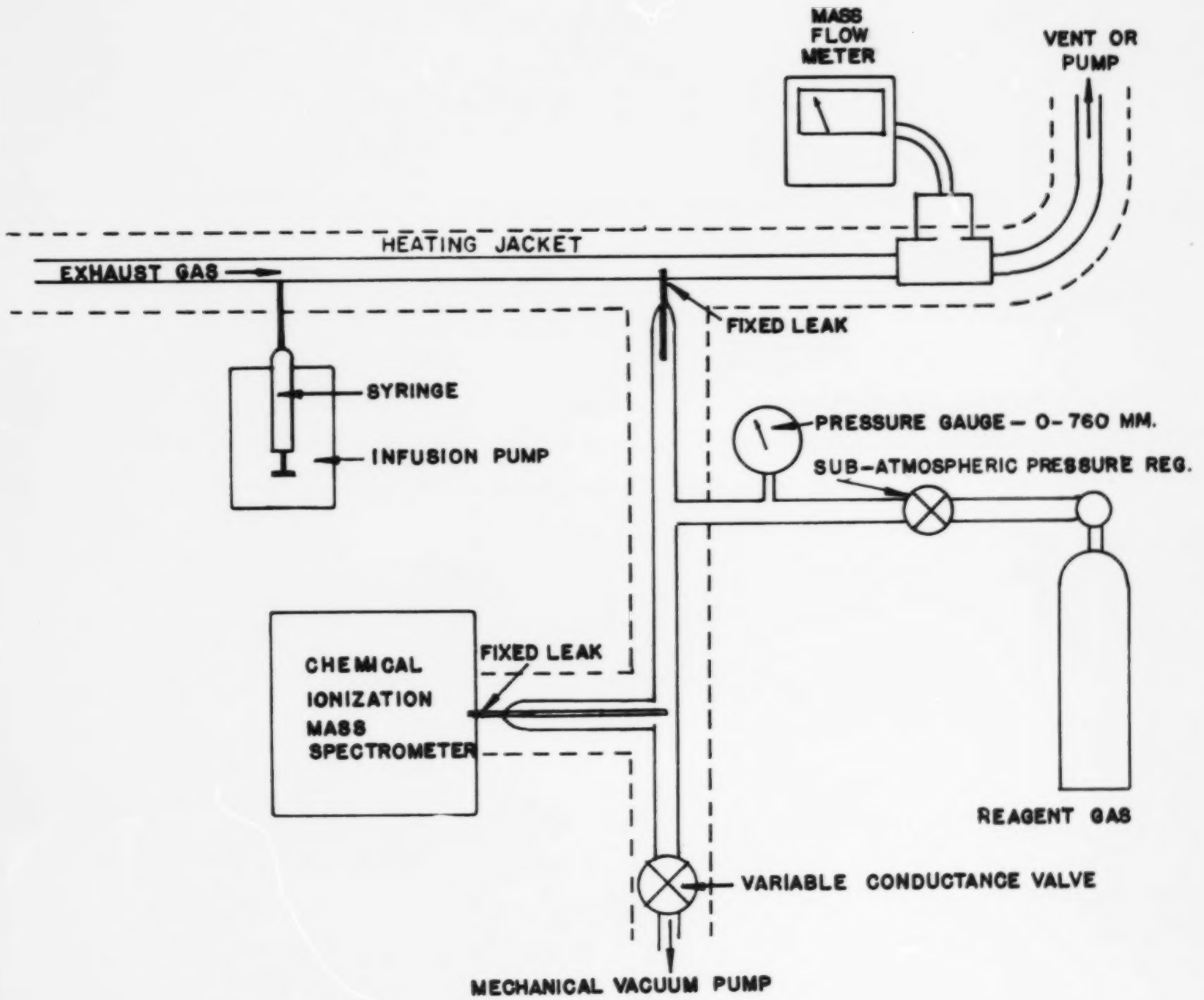


Figure 7

Schematic Diagram Of The Sample Inlet And Calibration System For The Prototype System For Analysis Of Oxygenated Hydrocarbons In Engine Exhaust.

leak. A second fixed leak connects the glass manifold to the chemical ionization mass spectrometer. The reagent gas is metered into the glass manifold through a sub-atmospheric pressure gas regulator. The total pressure in the glass manifold may be adjusted by using a variable conductance valve between the manifold and a mechanical vacuum pump. This valve serves as a fine control on the pressure in the manifold and hence the pressure in the chemical ionization mass spectrometer.

Calibration

The inlet system was designed to allow rapid calibration of the entire prototype system. A sample of artificial exhaust gas or inert gas is passed through the main exhaust gas line at a high flow rate, typically 15 litres per minute. A sample of aldehyde or ketone, or other compound for which a calibration measurement is required, is placed in the syringe and fixed in position on the infusion pump. With a known infusion rate and a known flow rate of the exhaust gas, precise mixtures at the ppm level can be obtained. A sample of this mixture is drawn into the glass manifold where the reagent gas is added in a proportion which can be read from the absolute pressure gauge provided and the resulting mixture analyzed in the chemical ionization mass spectrometer. The entire inlet system is operated hot (typically 150°C) during calibration measurements in an attempt to avoid errors due to condensation or polymerization on the walls.

This same inlet system is also used in the actual exhaust measurements. With the syringe and infusion pump in place, the calibration for a particular compound can be checked at any time by injecting that compound at a known rate into the exhaust gas stream.

RESULTS AND DISCUSSIONS

Chemical ionization mass spectral measurements have been carried out on a number of aldehydes and ketones. In most of this work methane was used as the reagent gas but experiments have also been carried out using propane, iso-butane, neo-pentane, and water as reagents. The mass spectra obtained in a series of measurements using methane are given in Figures 8 through 25. The relative sensitivities observed in these measurements are summarized in Table II.

These measurements were carried out using a cold inlet system and some of the variations in the sensitivities observed are probably due to difficulties with the inlet system. Also some of the spectra show residual contamination from compounds run in the previous measurements. When high concentrations of the sample were used, for example, Run No. 2 on crotonaldehyde, Run No. 1 on benzaldehyde and Run No. 13 on acetaldehyde, some reduction in the sensitivity is observed as a result of using up a significant amount of the methane reactant ions. Below concentrations of about 300 parts per million this effect is not observed and it is expected that the signal should be linear with concentration at lower concentrations. With the exception of Run No. 17 this series of measurements was conducted at a source pressure of 1 torr, source temperature of 150°C, and electron emission of 400 microamps.

The aldehyde-methane mixtures were prepared on a stainless steel vacuum line. A sample of liquid reagent grade aldehyde was expanded into the evacuated line and the pressure measured with a mechanical manometer. A small sample of the vapor (0.5 cc) was isolated and then further expanded into an evacuated 500 cc glass bulb. The glass

TABLE II: RELATIVE SENSITIVITIES MEASURED IN A SERIES OF CHEMICAL IONIZATION MEASUREMENTS ON ALDEHYDES AND KETONES USING METHANE REAGENT.

Run No.	Compound	Molecular Weight	Concentration (ppm)	Sensitivity mv/ppm) M+1	Total
13	Acetaldehyde	44	350	24	24.4
15	Acrolein	56	140	69	70
6	Propionaldehyde	58	270	27	28
14	Acetone	58	270	36	37
12	Crotonaldehyde	70	80	29	31
2	Crotonaldehyde	70	40,000	0.3	0.4
7	n-Butyraldehyde	72	200	6	19
5	iso-Butyraldehyde	72	35	80	108
11	2-Butanone	72	55	33	34
10	n-Valeraldehyde	86	50	5	19
9	iso-Valeraldehyde	86	40	2	15
8	2-Pentanone	86	60	20	21
3	3-Pentanone	86	100	10	11
4	Ethyl butyraldehyde	100	30	8	33
1	Benzaldehyde	106	1300	4.5	5

bulb was then filled with methane to 1 atmosphere of pressure. By this technique the concentration of the aldehyde in the methane is given by

$$C = \frac{V_1}{V_2} \cdot \frac{P_1}{P_2} \simeq \frac{1}{1000} \cdot \frac{P_1}{14.7}$$

Where V_1 is the volume before expansion, V_2 is the total volume, including the 500 cc bulb, P_1 is the measured pressure of the aldehyde vapor in psia and P_2 is the methane pressure. In using this static sample preparation it is possible that the actual final concentration of aldehyde may be somewhat lower than calculated if sufficient time for equilibration is not allowed. However, the concentration should not be higher than calculated.

The measurement on formaldehyde used Baker analyzed reagent grade formalin solution containing 37.8% HCHO stabilized with 13.1% methanol. The methane chemical ionization spectrum for this mixture is given in Figure 8. The concentration of formaldehyde in this sample was approximately 1000 ppm. The protonated formaldehyde ion is at mass 31 and the protonated methanol ion is at mass 33. The only interference with the protonated formaldehyde that is expected to occur is the double C^{13} isotope peak from $C_2H_5^+$; this may limit the detection limit for formaldehyde to about 0.1 ppm.

The chemical ionization spectrum for 1300 ppm benzaldehyde in methane reagent is given in Figure 9. The principal benzaldehyde ion is P+1 at mass 107. Impurity peaks from the earlier run on formalin solution are visible at masses 31 and 33. It may be noted that the mass 17 peak from methane is rather small compared to the other peaks in

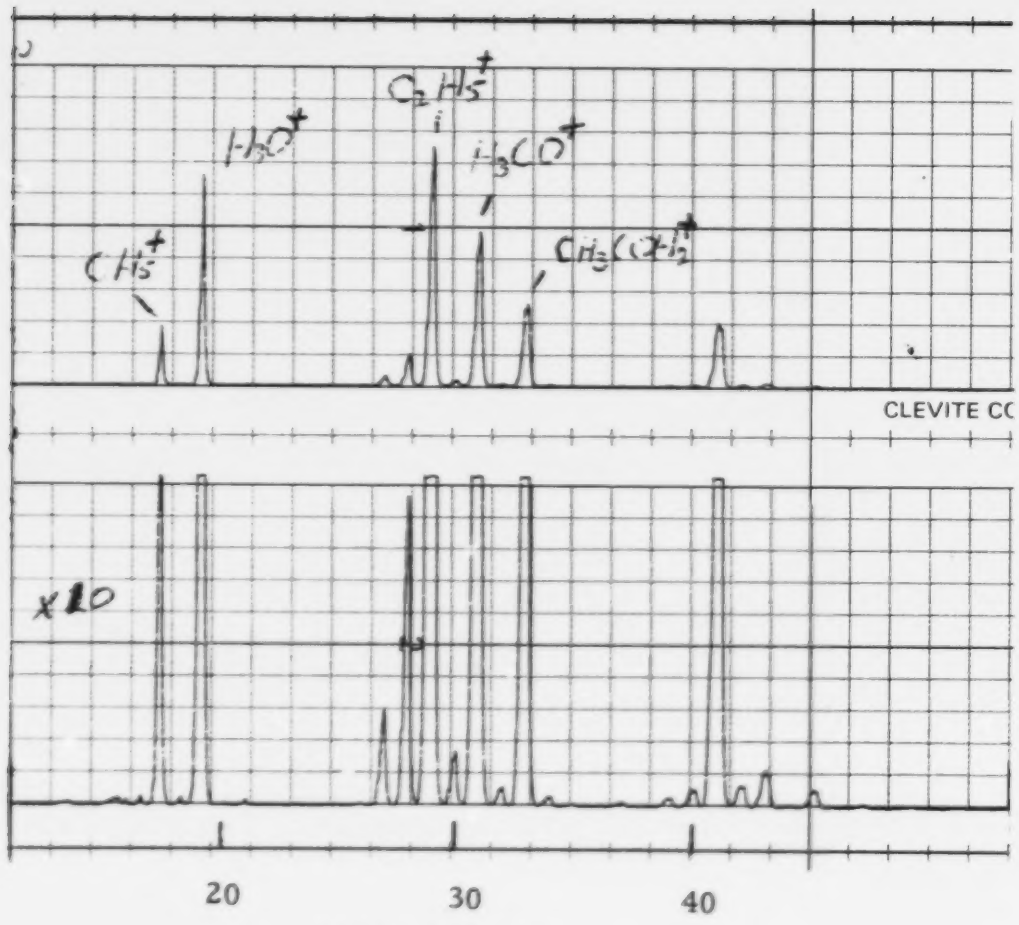


Figure 8. Chemical Ionization Mass Spectrum for Formalin Solution with Methane Reagent at 1 torr and 150°C.

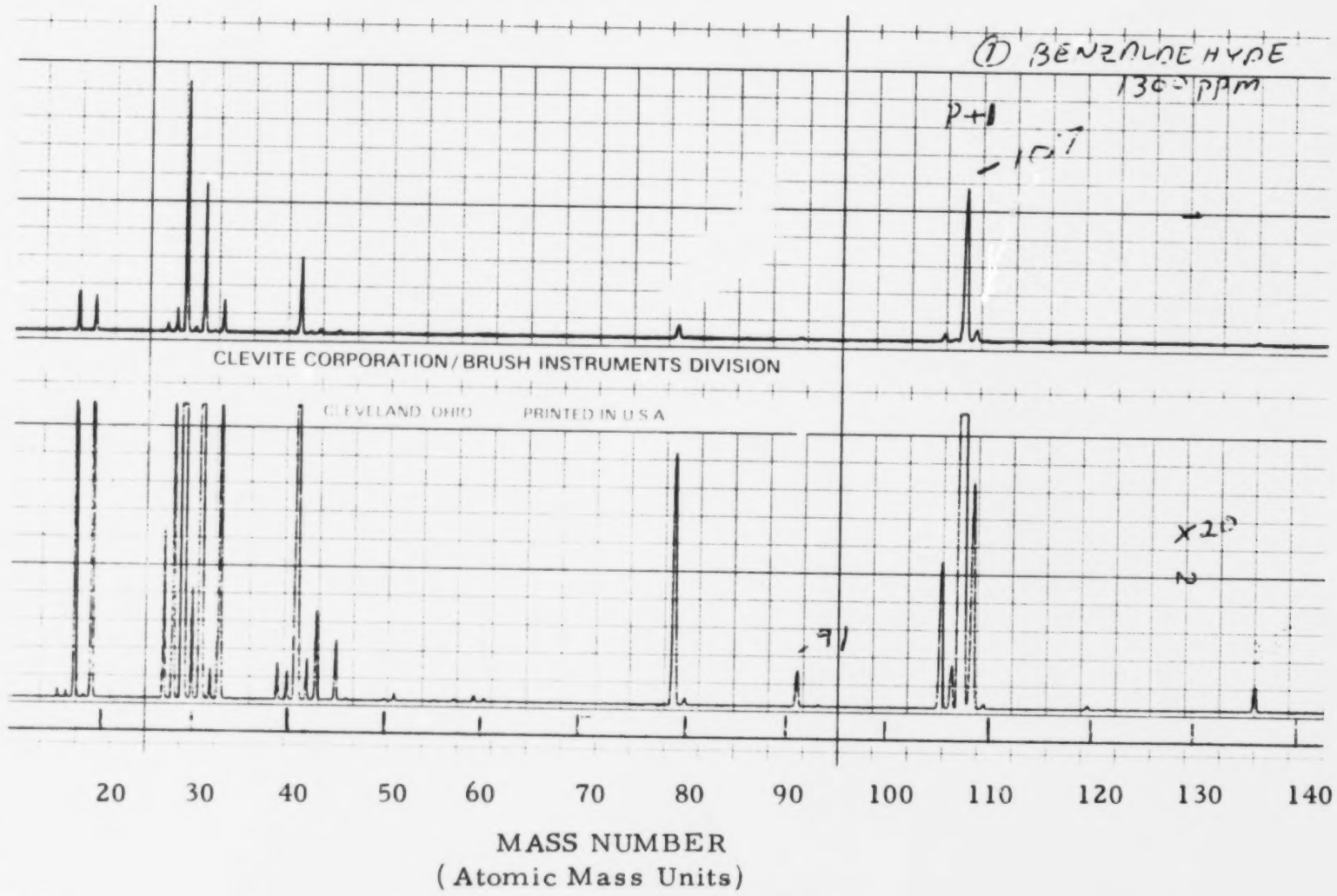


Figure 9 Chemical Ionization Mass Spectrum for Benzaldehyde with Methane Reagent at 1 torr and 150°C, Run Number 1.

the spectrum, indicating that a substantial fraction of the reagent ions have been used up by reaction at this concentration of benzaldehyde.

The chemical ionization spectrum for 4% crotonaldehyde in methane reagent is given in Figure 10. The major crotonaldehyde peaks in this result are the P+1 at mass 71, and the P-1 at mass 69. A significant amount of the protonated dimer ion is observed at mass 141. At this relatively high sample concentration, it may be noted that the methane reagent ions have virtually disappeared.

The chemical ionization spectrum for 100 ppm of 3-pentanone in methane reagent is given in Figure 11. The only significant peak produced from the 3-pentanone is the P+1 ion at mass 87. Impurity peaks from the early runs of benzaldehyde and formalin solution are visible at masses 107, 71, 33, and 31.

The chemical ionization mass spectrum in 30 ppm of ethyl butyraldehyde in methane reagent is given in Figure 12. The principal ions produced from the ethyl butyraldehyde are the P+1 ion at mass 101 and the fragment ion produced by loss of water from the protonated parent mass 83. The ion at mass 59 may be due either to loss of C_3H_6 from the protonated parent or due to a significant impurity of either propionaldehyde or acetone in the sample. The other ions in the spectrum are due principally to impurities residual from the previous samples.

The chemical ionization mass spectrum for 35 ppm of iso-butyraldehyde in methane reagent is given in Figure 13. The principal ion produced from the iso-butyraldehyde is the P+1 at mass 73. Fragment ions due to loss of H_2 and loss of water from the protonated parent are observable at masses 71 and 55 respectively.

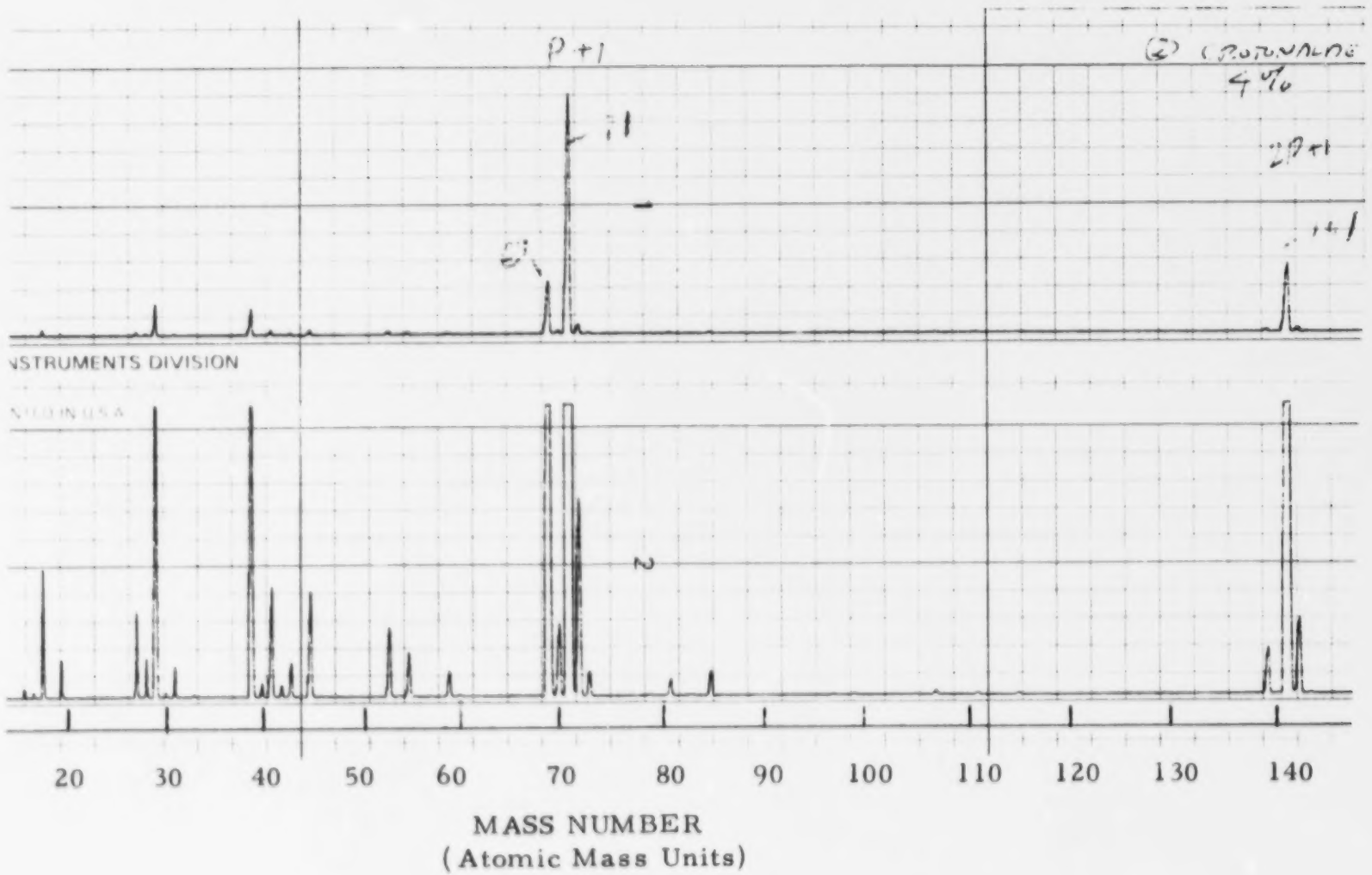


Figure 10. Chemical Ionization Mass Spectrum for Crotonaldehyde with Methane Reagent at 1 torr and 150°C, Run 2.

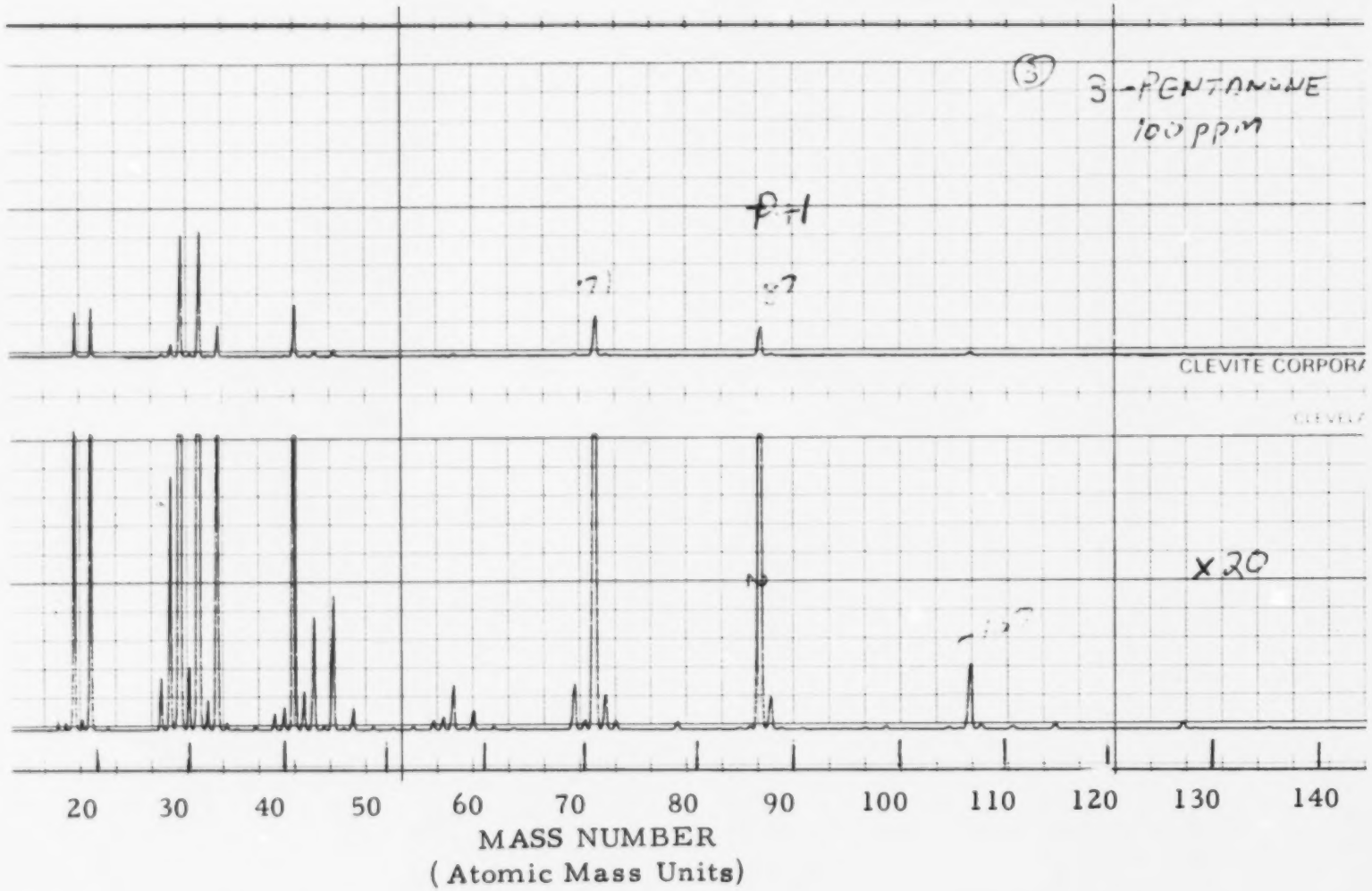


Figure 11. Chemical Ionization Mass Spectrum for 3-Pentanone with Methane Reagent at 1 torr and 150°C, Run Number 3.

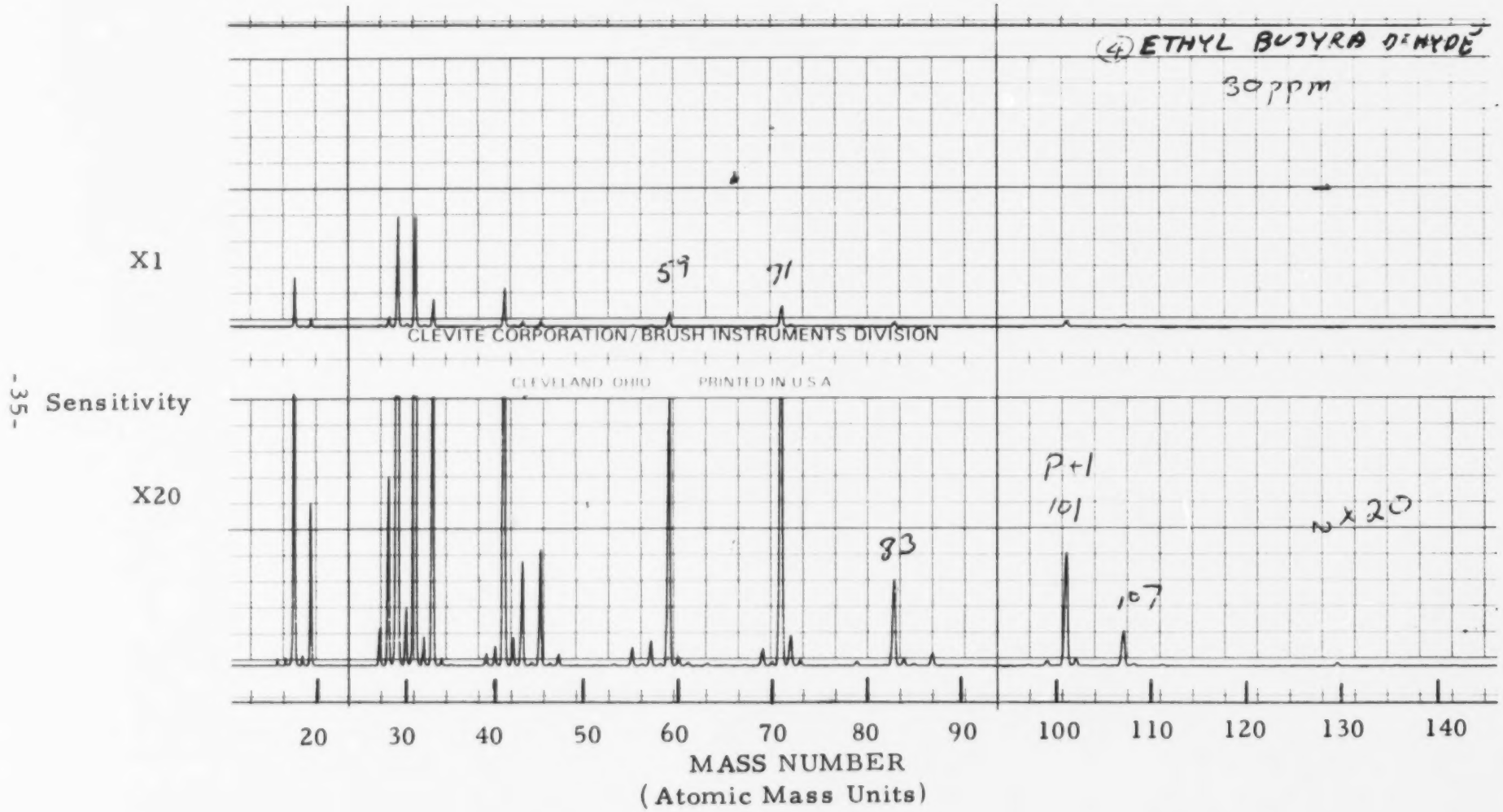


Figure 12. Chemical Ionization Mass Spectrum for Ethyl Butyraldehyde with Methane Reagent at 1 torr and 150°C, Run Number 4.

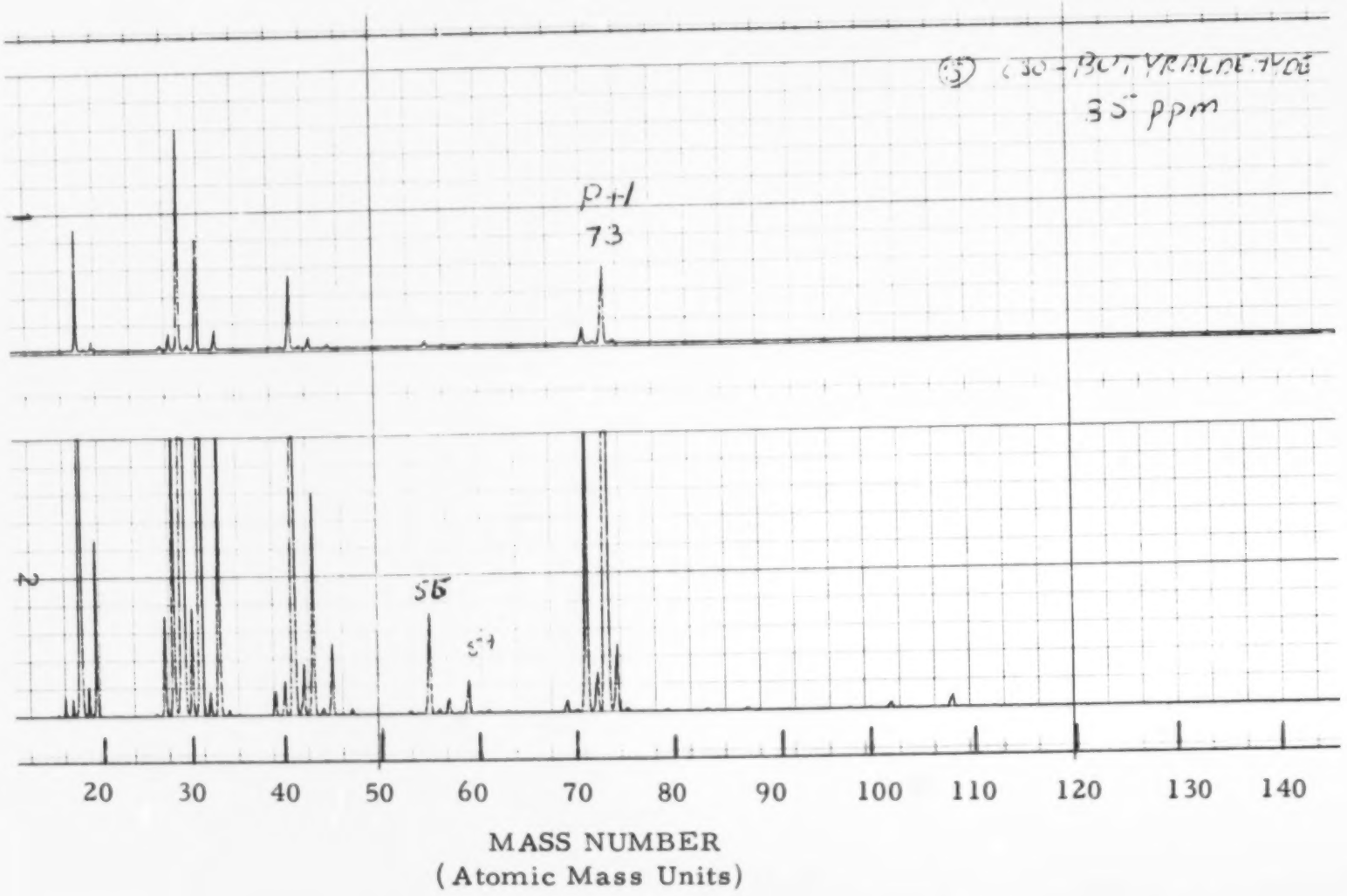


Figure 13. Chemical Ionization Mass Spectrum for iso-Butyraldehyde with Methane Reagent at 1 torr and 250°C, Run Number 5.

The chemical ionization mass spectrum for 270 ppm of propionaldehyde in methane reagent is given in Figure 14. The principal ion produced from the propionaldehyde is the P+1 at mass 59. A small amount of the protonated dimer ion is observed at mass 117.

The chemical ionization mass spectrum for 200 ppm of n-butyraldehyde in methane reagent is given in Figure 15. The protonated parent ion occurs at mass 73 and in this case the fragment ion due to loss of water at mass 55 is larger than the protonated parent ion. It is unlikely that the large peak at mass 59 is due to fragments of the benzaldehyde fragment ions but is probably either propionaldehyde residue left from the previous sample or due to a significant impurity of either propionaldehyde or acetone in the butyraldehyde sample.

The chemical ionization mass spectrum for 60 ppm of 2-pentanone in methane reagent is given in Figure 16. The principal ion produced from the 2-pentanone is the P+1 at mass 87. The other ions in the spectrum are probably due to residual impurities in the previous samples.

The chemical ionization mass spectrum for 40 ppm of iso-valeraldehyde in methane reagent is given in Figure 17. The P+1 ion occurs at mass 87 but the fragment ion due to loss of water from the protonated parent at mass 69 is larger in intensity.

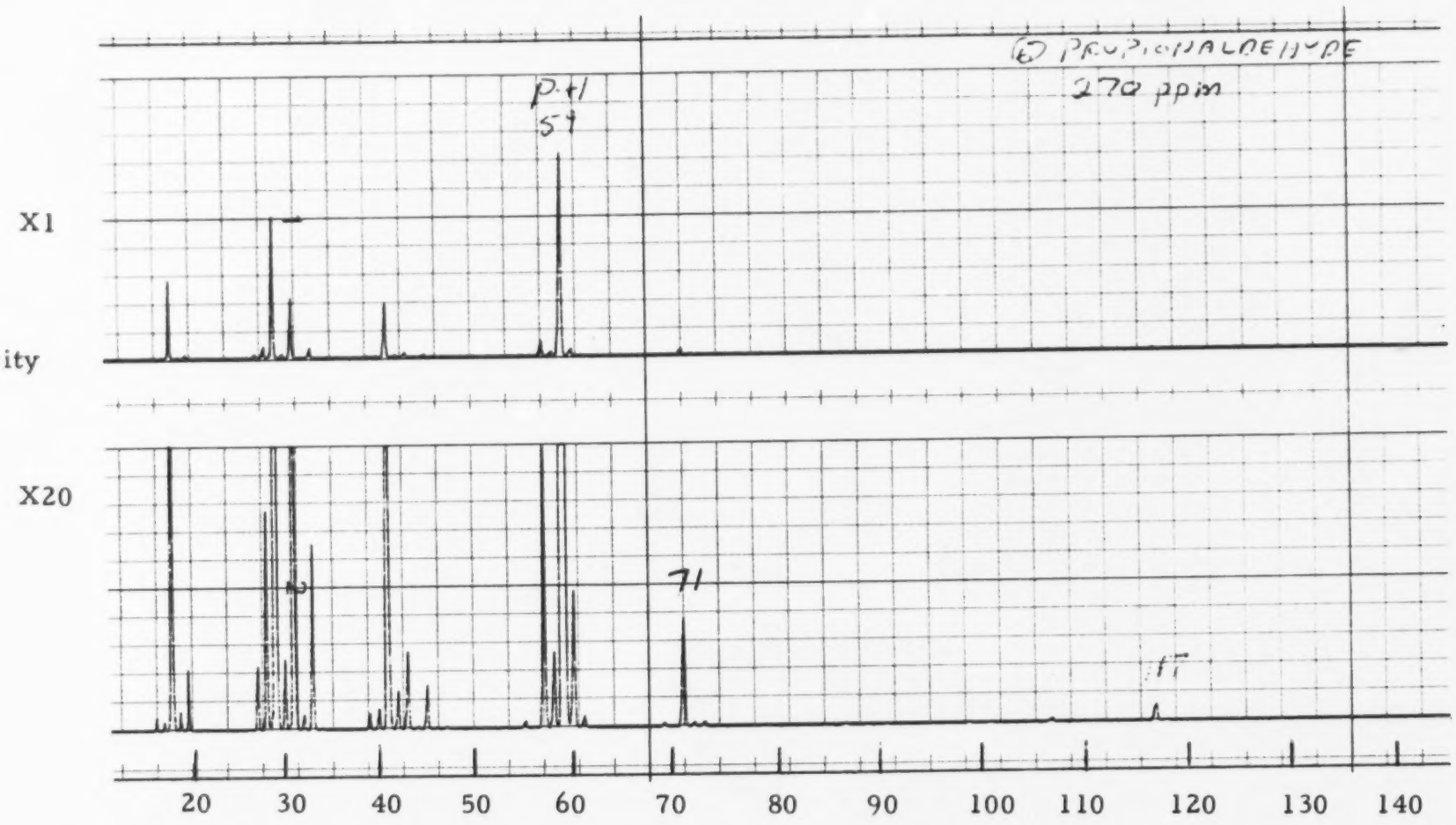


Figure 14. Chemical Ionization Mass Spectrum for Propionaldehyde with Methane Reagent at 1 torr and 150°C, Run Number 6.

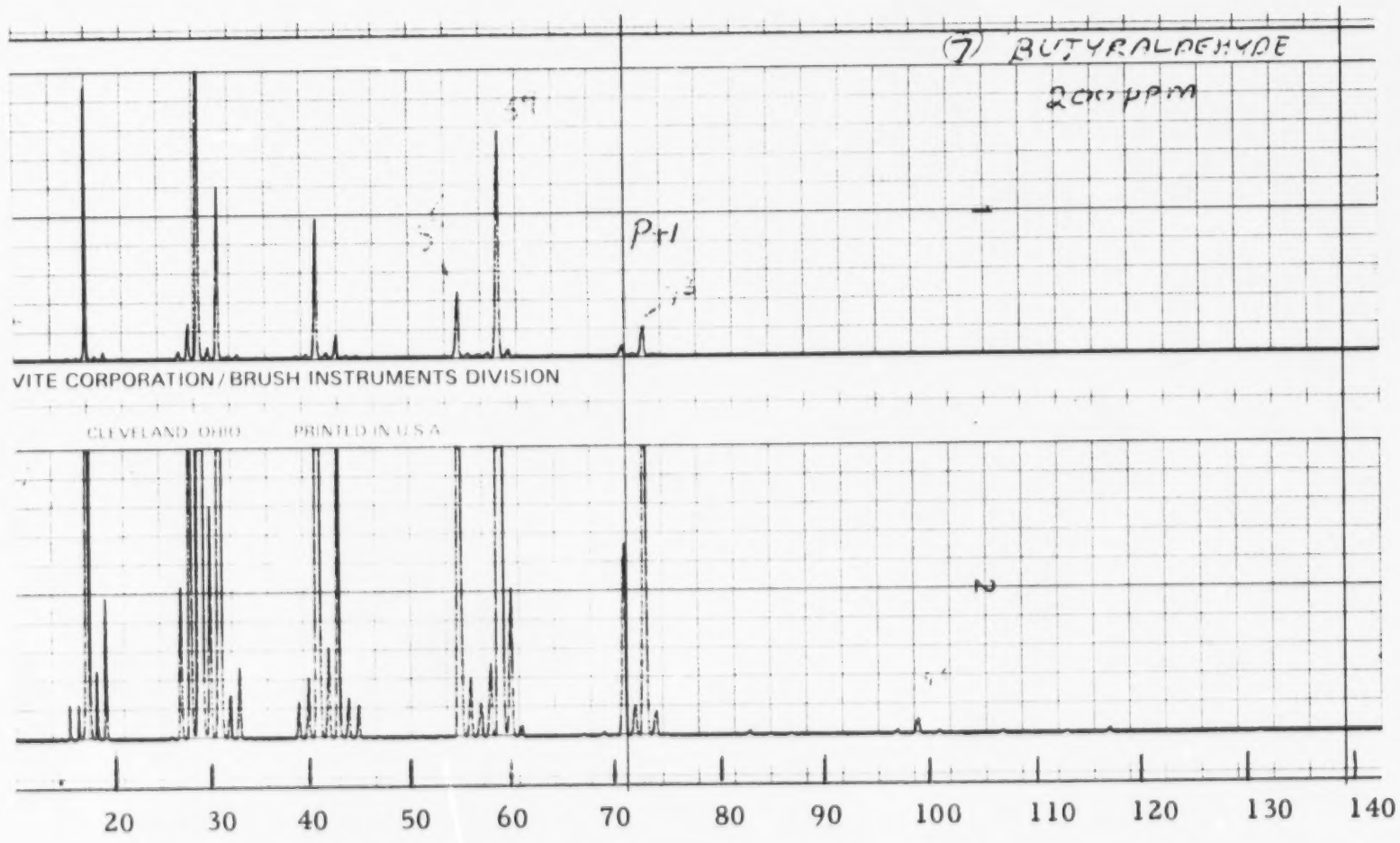


Figure 15. Chemical Ionization Mass Spectrum for Butyraldehyde with Methane Reagent at 1 torr and 150°C, Run Number 7.

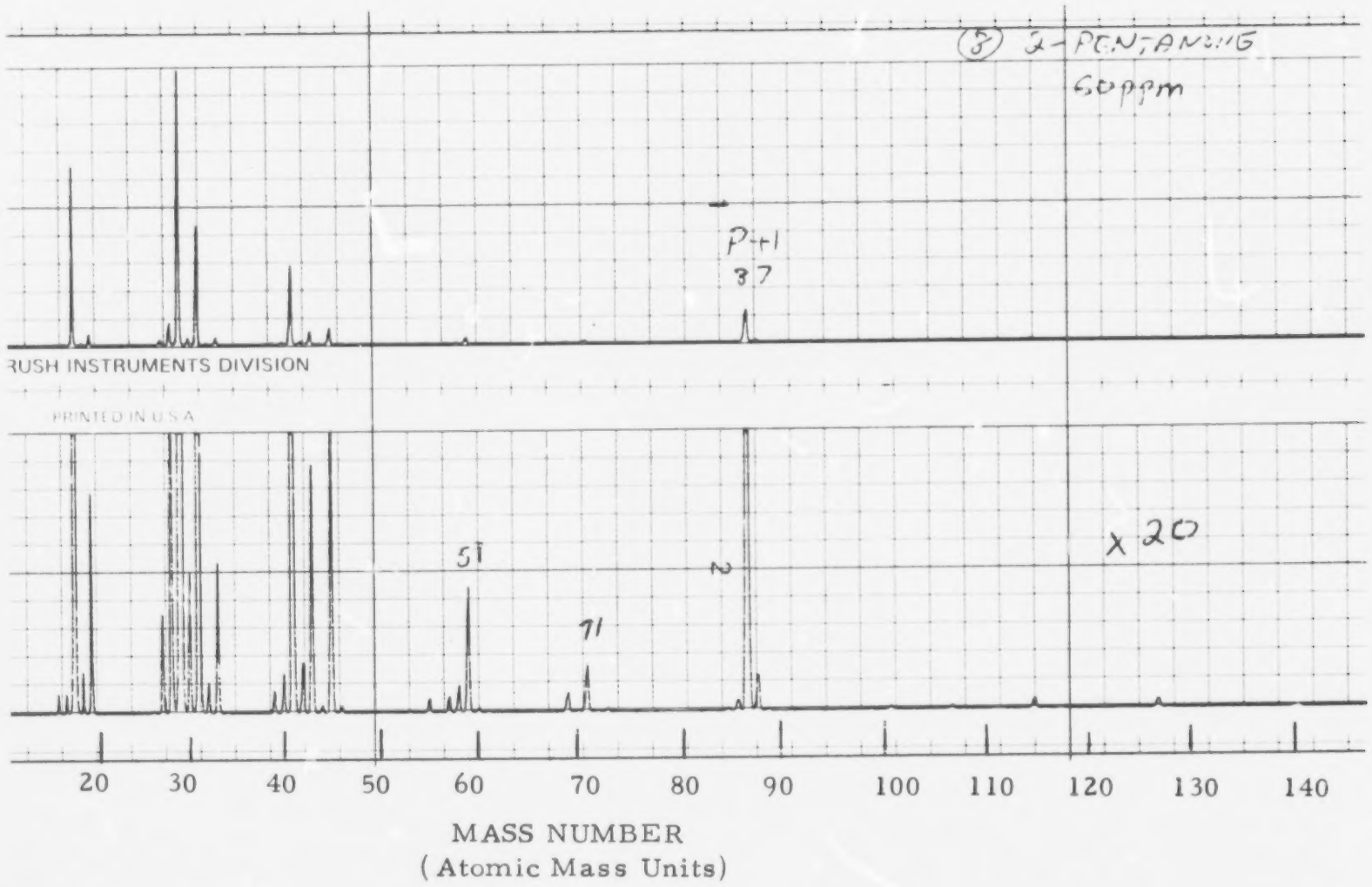


Figure 16. Chemical Ionization Mass Spectrum for 2-Pentanone with Methane Reagent at 1 torr and 150°C, Run Number 8.

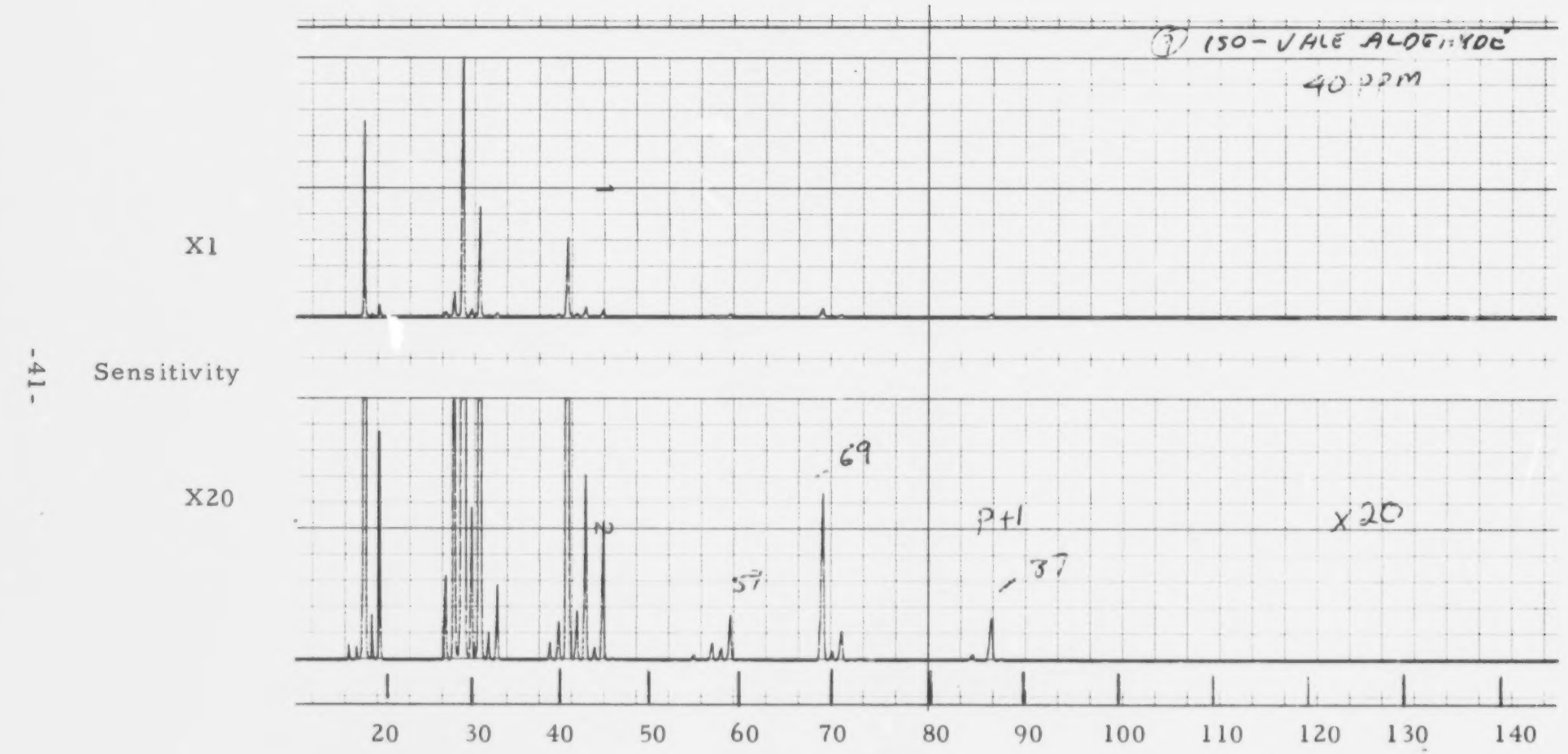


Figure 17. Chemical Ionization Mass Spectrum for iso-Valeraldehyde with Methane Regant at 1 torr and 150°C, Run Number 9

The chemical ionization mass spectrum for 50 ppm n-valyraldehyde in methane reagent is given in Figure 18. The protonated parent ion is at mass 87 and again the fragment ion at mass 69 due to loss of water from the protonated parent ion is more intense than the P+1 ion.

The chemical ionization mass spectrum for 55 ppm for 3-butanone in methane reagent is given in Figure 19. The only significant ion produced from the 3-butanone is the P+1 ion at mass 73.

The chemical ionization mass spectrum for 80 ppm of crontonaldehyde in methane reagent is given in Figure 20. The only ion produced from the crotonaldehyde is the P+1 ion at mass 71. This measurement is a repeat of the earlier measurement at higher concentrations of the crotonaldehyde given in Figure 10 and represents the mass spectrum obtained under analytic conditions.

The chemical ionization mass spectrum for 350 ppm of acetaldehyde in methane is given in Figure 21. The principal ion produced from the acetaldehyde is the protonated parent at mass 45. A small amount of the protonated dimer ion is observed at mass 89.

The chemical ionization mass spectrum for 270 ppm of acetone in methane reagent is given in Figure 22. The protonated parent ion occurs at mass 59 and no significant fragment ions are observed. A small amount of the protonated dimer ion is observed at mass 117 and a fragment due to loss of water from the protonated dimer at mass 99.

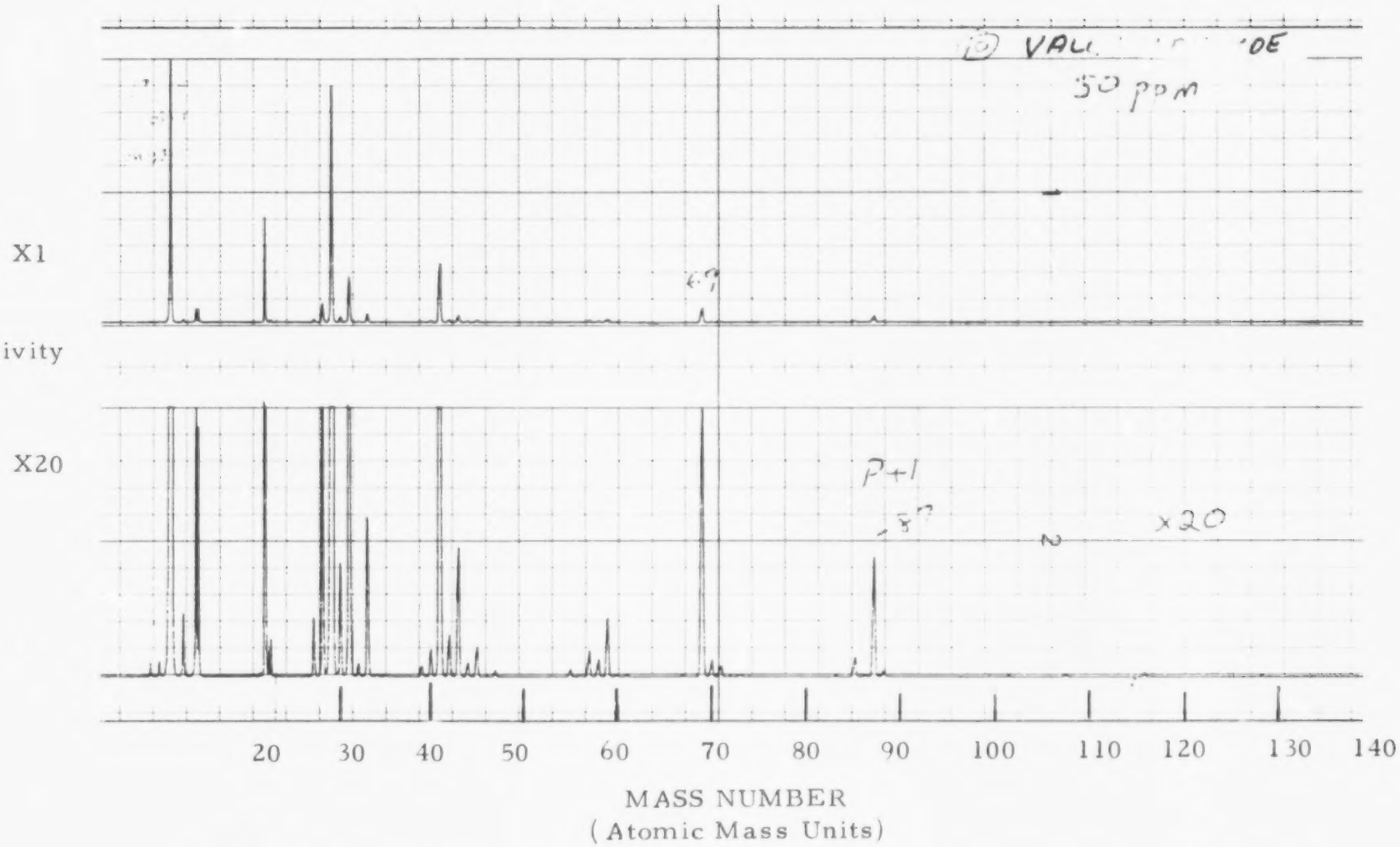


Figure 18. Chemical Ionization Mass Spectrum for Valeraldehyde with Methane Reagent at 1 torr and 150°C, Run Number 10

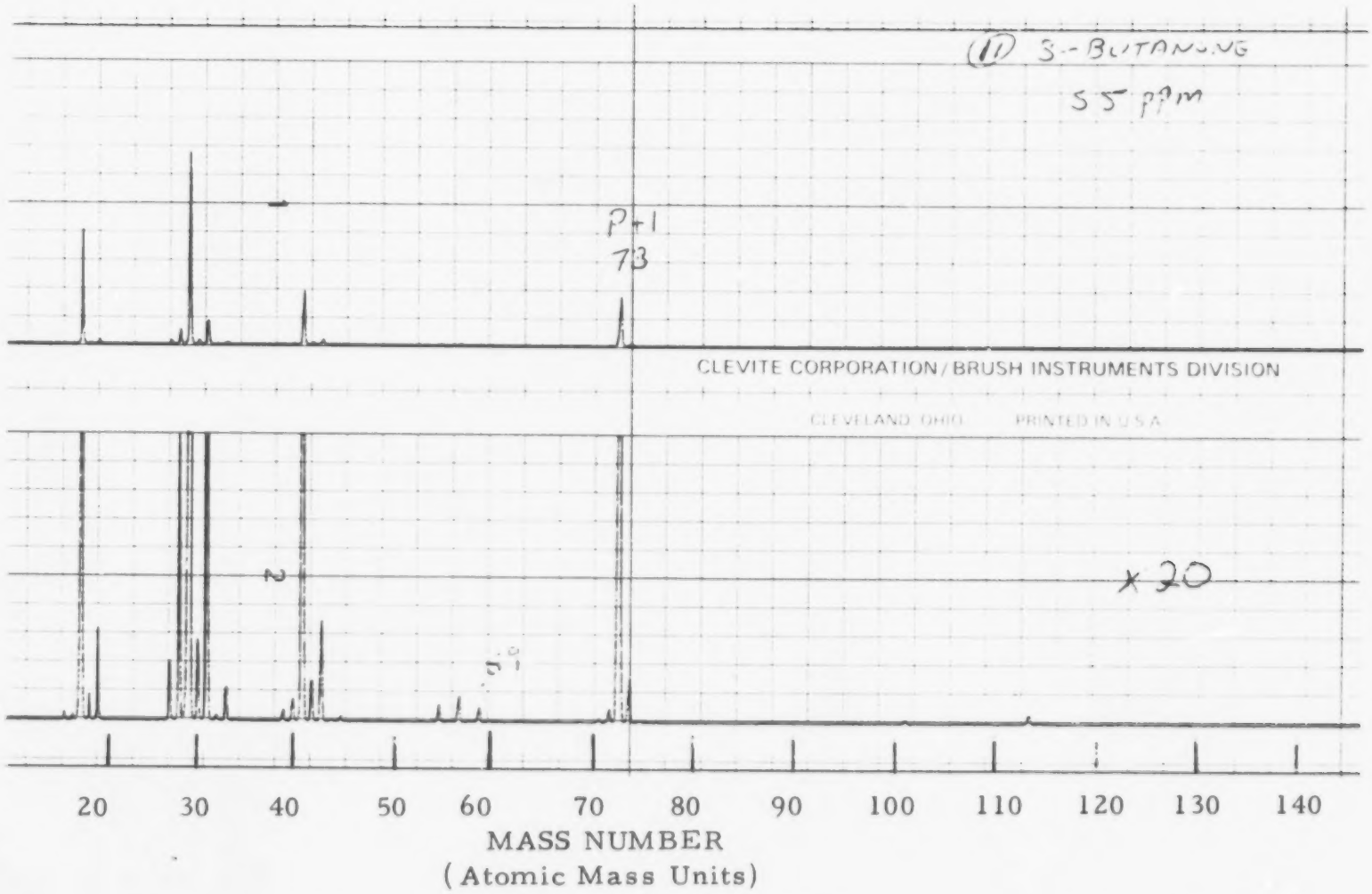
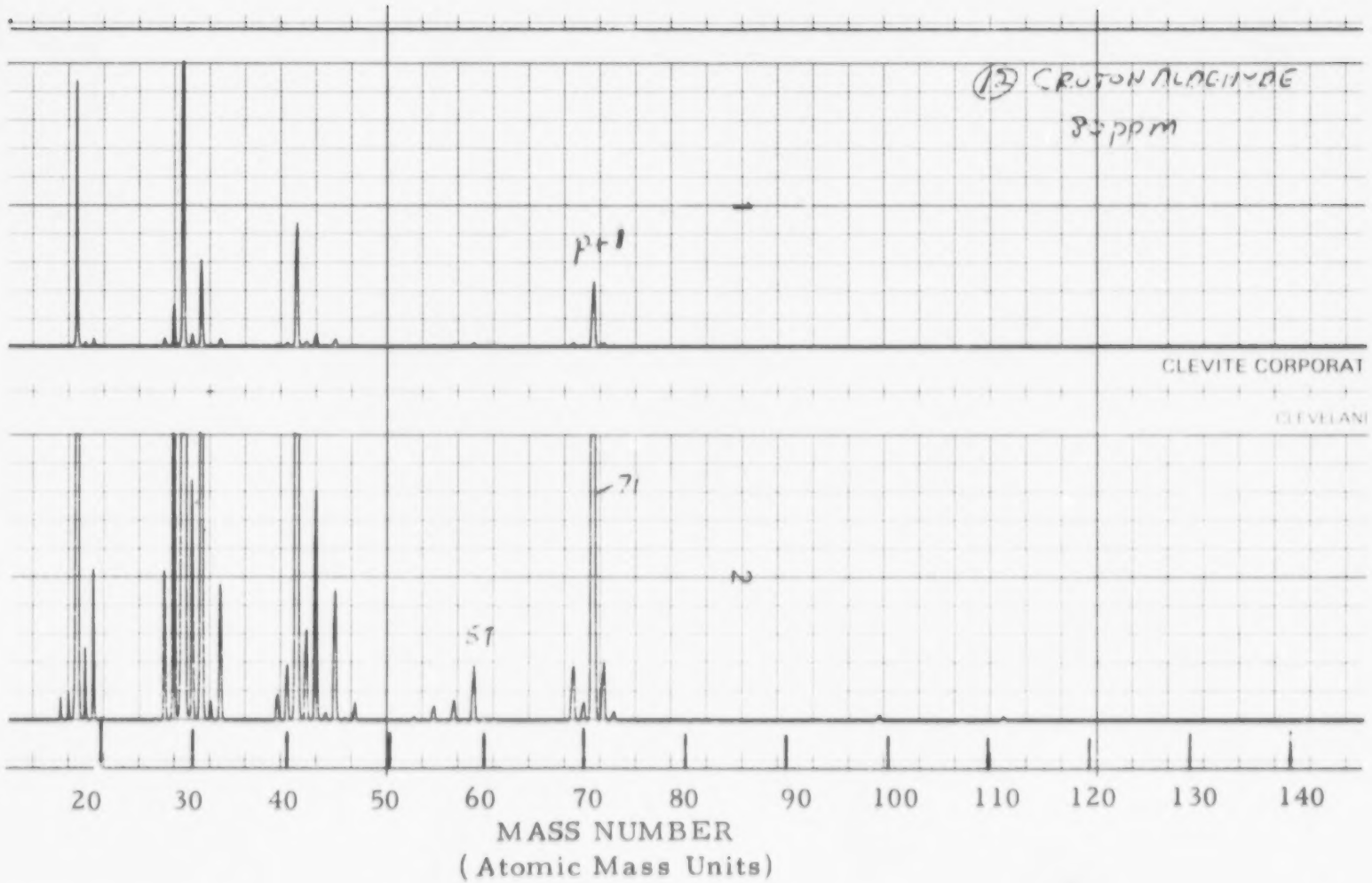


Figure 19. Chemical Ionization Mass Spectrum for 3-Butanone with Methane Reagent at 1 torr and 150°C, Run Number 11.



X1

Sensitivity

X20

Figure 20. Chemical Ionization Mass Spectrum for Crotonaldehyde with Methane Reagent at 1 torr and 150°C, Run Number 12.

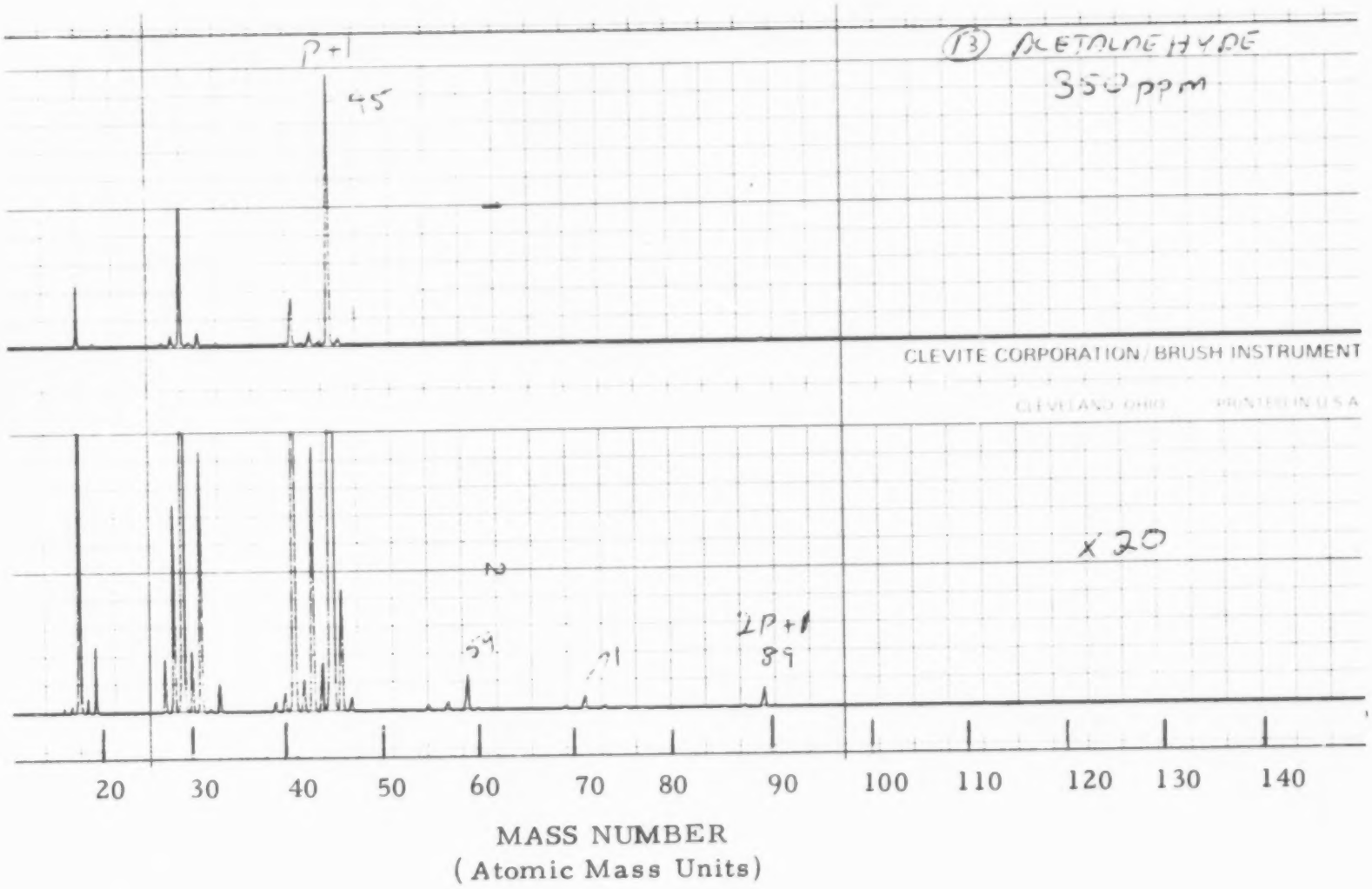


Figure 21. Chemical Ionization Mass Spectrum for Acetaldehyde with Methane Reagent at 1 torr and 150°C, Run Number 13.

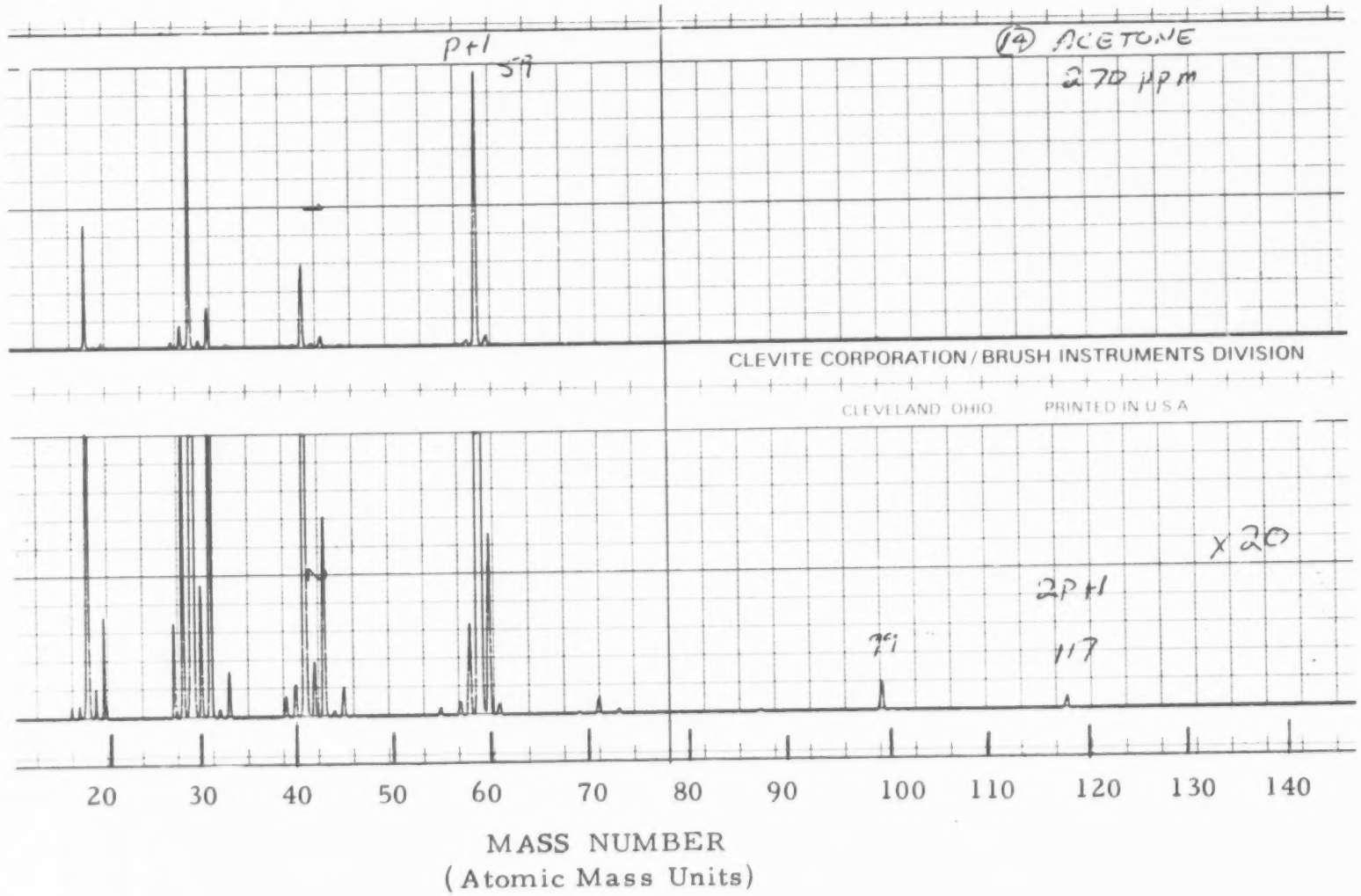


Figure 22. Chemical Ionization Mass Spectrum for Acetone with Methane Reagent at 1 torr and 150°C, Run Number 14

The chemical ionization mass spectrum for 140 ppm of acrolein in methane reagent is given in Figure 23. The principal ion in the spectrum is the P+1 at mass 57. A very small amount of the dimer ion at mass 113 is also observed. No significant fragment ions are observed from the acrolein.

The chemical ionization mass spectrum for a methane blank run immediately following the preceding runs is given in Figure 24. This measurement was done virtually under the same conditions as the preceding runs on the aldehydes. The bottom trace on Figure 24 corresponds to increasing the sensitivity by both increasing the electron beam current by a factor of six and increasing the recorder sensitivity by a factor of ten. This result shows the noise level of the instrument and indicates that a few parts per billion of the aldehydes should be detectable at the highest sensitivity.

Run No. 17 (Figure 25) was carried out to assess the sensitivity of the chemical ionization method. The source pressure was increased for this run to 5 torr and the electron emission was increased to 2 milliamps. In this measurement a sample consisting of 2 ppm of benzaldehyde in methane was used. The signal for the M+1 ion (mass 107) was 600 millivolts per ppm of benzaldehyde. The noise level was two millivolts rms. This measurement indicates that a concentration of 10 parts per billion of benzaldehyde would give a signal-to-noise ratio greater than 3.

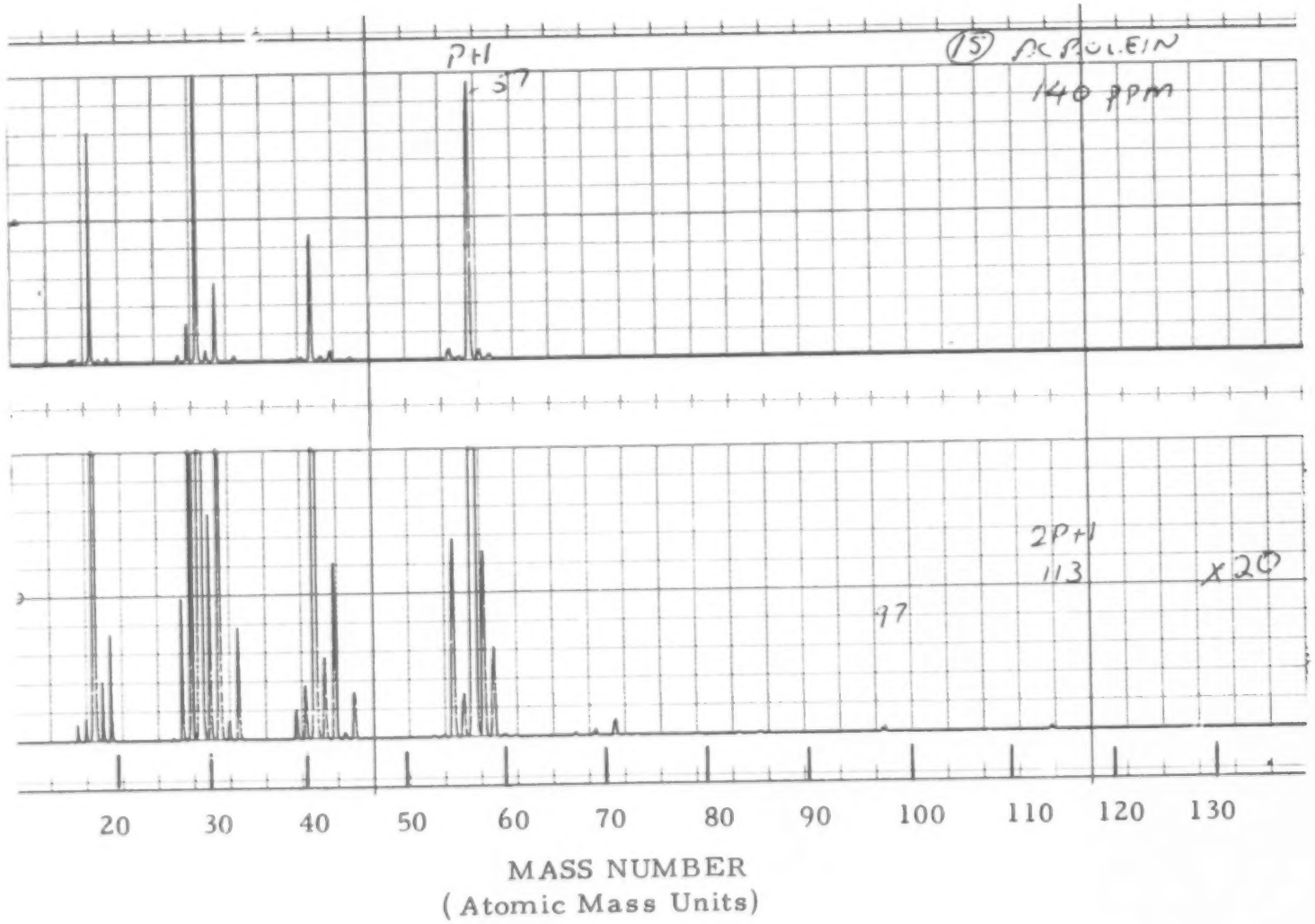


Figure 23. Chemical Ionization Mass Spectrum for Acrolein with Methane Reagent at 1 torr and 150°C, Run Number 15.

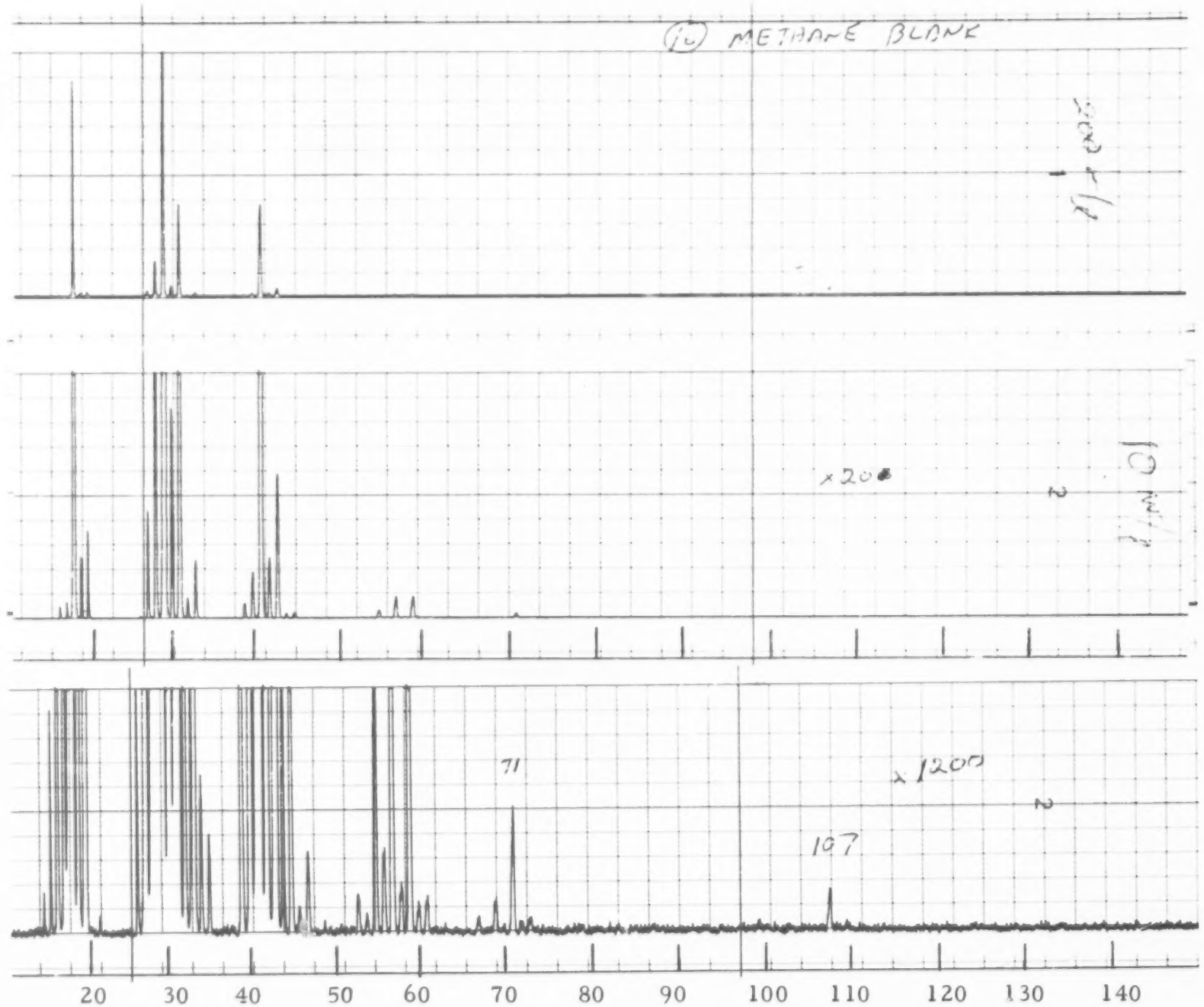


Figure 24. Chemical Ionization Mass Spectrum for Methane Blank at 1 torr and 150°C, Run Number 16.

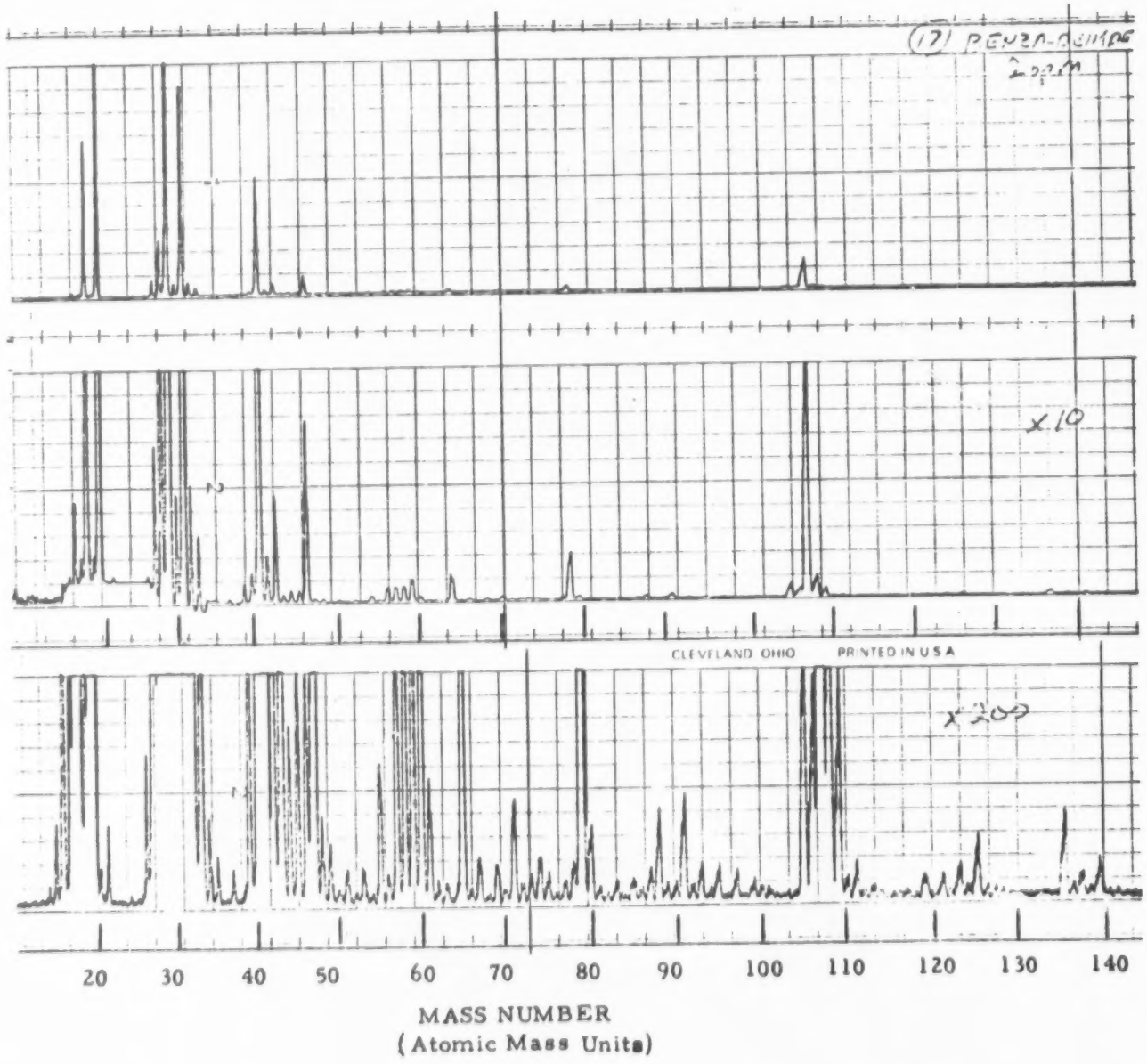


Figure 25. Chemical Ionization Mass Spectrum for Benzaldehyde at 1 torr and 150°C, Run Number 17.

In the absence of interference and fragmentation it is expected that the sensitivity for the other aldehydes and ketones should be comparable. The larger saturated aldehydes; butyraldehyde, valeraldehyde, and ethyl butyraldehyde, all show substantial fragmentation of the M+1 ion produced by proton transfer from methane reagent ions. These fragmentations, which involve loss of hydrogen molecule and loss of water molecule as the principal reactions, do not occur to any appreciable extent for the isomeric ketones studied. The fragment ions corresponding to loss of H_2O and H_2 may be used to distinguish between the aldehydes and ketones. These fragmentations cause the sensitivity, as determined from the M+1 ion intensity, to be somewhat lower for the larger saturated aldehydes than for the other compounds studied.

The saturated aldehydes and ketones do not suffer from interference with the hydrocarbons present. The oxygenated compounds give ions principally at the parent mass plus 1, while the hydrocarbons of the same molecular weight yield principal ions at the parent mass minus 1. The protonated alkanes larger than ethane are apparently not stable and the protonated species have not been observed in the mass spectrometer. On the other hand, the unsaturated aldehydes, e.g. acrolein and crotonaldehyde, are interfered with by the C_4 and C_5 hydrocarbons respectively. Butyl ions at mass 57 may be produced by proton transfer to the butenes and by hydride ion transfer from the butanes. These reactions produce ions of the same nominal mass as the protonated acrolein.

It appears likely that a different reagent will be required for the measurement of the unsaturated aldehydes in engine exhaust. Additional experimental data is needed to choose an appropriate reagent. One possibility is ammonia which will produce NH_4^+ as the principal reagent ion. This ion may transfer a proton to acrolein and not to the butenes. However, NH_4^+ will certainly not react with formaldehyde. Thus it may be necessary to do the analysis ir two steps; using methane to measure the saturated aldehydes and using a different reagent to measure the unsaturated aldehydes. Further experimental work will be undertaken to establish the reagent and operating conditions with which acrolein can be analyzed in engine exhaust by using the chemical ionization technique.

The results of the present work indicate that the chemical ionization direct reading mass spectrometer can be used to monitor individual saturated aldehydes and ketones in engine exhaust in the concentration range from 10 parts per billion to 300 parts per million. Further work is required to fully establish the sensitivity, accuracy, and specificity of this technique in the application to routine exhaust measurements. Additional work is also required to extend the technique to unsaturated aldehydes and to other components of interest.

APPENDIX

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